An International Journal of Analytical Chemistry

ταλαντα

talanta

PERGAMON PRESS
OXFORD · LONDON · NEW YORK · PARIS

✓1964 VOLUME 11 MARCH


EASILY AND QUICKLY

SUMMARIES FOR CARD INDEXES

The determination of the oxidation states of tracer uranium, neptunium and plutonium in aqueous media: S. C. Foti and E. C. Freiling, *Talanta*, 1964, **11**, 385. (U. S. Naval Radiological Defense Laboratory, Chemical Technology Division, San Francisco, California, U.S.A.)

Summary—This report describes the development, testing and application of a chemical procedure for determining the distributions of uranium, neptunium and plutonium among their respective oxidation states in various aqueous media at tracer concentrations. The separations achieved are of the order of 95% clean. Results are presented which show the per cent extraction of uranium, neptunium and plutonium oxidation states by $0{\cdot}4M$ 2-thenoyltrifluoracetone at various values of pH, and per cent carried by lanthanum fluoride from distilled water and sea water under various conditions. Radiochemical analysis of the separated fractions can then be used to determine the required oxidation state distributions.

Some observations on the zero-current behaviour of antimony indicator electrodes: E. Bishop and G. D. Short, *Talanta*, 1964, **11**, 393. (Washington Singer Laboratories, The University, Prince of Wales Road, Exeter, Devon, U.K.)

Summary—Methods are described for the preparation and handling of antimony electrodes of precise area and good reproducibility, and for the determination of potential-pH and potential-log P_{O_2} relationships under controlled conditions. Conditions affecting the response characteristics are defined and critically examined: they include the purity of the antimony, the history of the electrode, the temperature, agitation, poising, ionic strength and composition of the solution, the working pH range, the condition of the electrode surface and the oxygen content of the solution. The marked influence of the presence of buffering materials, of the condition of the electrode surface and of the oxygen content of the solution are emphasised. Phosphates cause changes of the electrode surface. The current situation is reviewed in the context of the present work, and electrode mechanisms are discussed.

Thermogravimetric and differential thermal analysis of europium^{III} oxalate and some europium^{II} salts: A. Glasner, E. Levy, M. Steinberg and W. Bodenheimer, *Talanta*, 1964, **11**, 405. (Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel.)

Summary—The differential thermal analysis curves of $Eu_2(C_2O_4)_3$, EuC_2O_4 and $EuCO_3$ exhibit prominent exothermic peaks in the region of 420° because of the oxidation of europium^{II} to europium^{III}. The first step in the decomposition of $Eu_2(C_2O_4)_3$, after completion of dehydration, is $Eu_2(C_2O_4)_3 \rightarrow 2EuC_2O_4 + 2CO_2$. The reasons for some conflicting differential thermal analysis curves of the rare earth oxalates obtained by various authors are explained. The europium^{II} oxalate, $EuC_2O_4{\cdot}1.7H_2O$, is prepared.

РЕЗЮМЯ

ОПРЕДЕЛЕНИЕ СТЕПНИ ОКИСЛЕНЯ СЛЕДОВ УРАНА, НЕПТУНИЯ И ПЛУТОНИЯ В ВОДНЫХ СРЕДАХ ПРИ ИНДИКАТОРНЫХ КОНЦЕНТРАЦИЙ:

S. C. Foti and E. C. Freiling, *Talanta,* 1964, **11,** 385.

Резюме—В данной работе описафно развитие, испитание и применение химического метода для определения степеней окисления урана, нептуния и плутония в разных водных средах при индикаторных концентраций. Получены сепарации ряда 95%. Результаты показывают процент экстракции валентных состояний урана, нептуния и плутония с 0,4 M раствором 2-тэноилтрифторацетона при различных pH, как и процент экстрагирован фтористым лантаном из дистиллированной и морской воды, в различных условиях. Радиохимический анализ выделённых фракций может затем послужить для определения искаемых распределений степеней окисления.

НЕКОТОРЫЕ ИССЛЕДОВАНИЯ СВОЙСТВ НУЛЕВОГО ТОКА СУРМЯННЫХ ИНДИКАТОРНЫХ ЭЛЕКТРОДОВ:

E. Bishop and G. D. Short, *Talanta,* 1964, **11,** 393.

Резюме—Описан метод приготовления и использования сурьмянных электродов точной площади и хорошой воспроизвомости, и для определения отношения потенциалов pH и —лог P_{O_2} в контроп ированых условиях. Было исследовано влияние: чистоты сурьмы, истории электрода, температуры, взбалтывания, отравления, ионной силы и состава раствора, рабочей pH области, поверхности электрода и содержания киспорода в растворе. Было найдено значительное влияние присутствия буфферных растворов, поверхности эпектрода и содержания кислорода в растворе. Фосфат является причиной изменения поверхности электрода. В работе рассматривается электродный механизм и современное состояние проблема.

ТЕРМОГРАВИМЕТРИЧЕСКИЙ И ДИФФЕРЕНЦИАЛЬНЫЙ ТЕПЛОВОЙ АНАЛИЗ ОКСАЛАТА ЭВРОПИЯ(III) И НЕКОТОРЫХ СОЛЕЙ ЭВРОПИЯ(II):

A. Glasner, E. Levy, M. Steinberg and W. Bodenheimer, *Talanta,* 1964, **11,** 405.

Резюме—Кривы дифференциального теплового анализа $Eu_2(C_2O_4)_3$, EuC_2O_4 и $EuCO_3$ показивают ясные экзотермические пики в области 420°, вследствие окисления Eu(II) в Eu(III). Первый шаг в разложении $Eu_2(C_2O_4)_3$—после оконченной дегидратации—$Eu_2(C_2O_4)_3 \rightarrow 2EuC_2O_4 + 2CO_2$. Обсняются причины некоторых противоречивых кривых дифференциального теплового анализа оксалатов редкоземельных элементов и сообщается приготовление оксалата эвропия(II), $EuC_2O_4 \cdot 1{,}7H_2O$.

An investigation of 2-amino-4-chlorobenzenethiol hydrochloride as a spectrophotometric reagent for the determination of molybdenum: GORDON F. KIRKBRIGHT and JOHN H. YOE, *Talanta*, 1964, **11**, 415. (Pratt Trace Analysis Laboratory, Department of Chemistry, University of Virginia, Charlottesville, Virginia, U.S.A.)

Summary—2-Amino-4-chlorobenzenethiol hydrochloride forms a green precipitate with molybdenum^{VI} at pH 2. The precipitate can be extracted into chloroform and has an absorbance maximum at 720 mμ. The sensitivity of the reaction is 0·0054 μg of molybdenum per cm^2 for log $I_0/I = 0{\cdot}001$. Development of the spectrophotometric method for the determination of molybdenum included a study of the effect of pH, reagent concentration, rate of complex formation and extraction, temperature and conformity to Beer's law. The method has been applied to the determination of molybdenum in steel and cast iron.

Photometric titrations—VII: The consecutive titration of cadmium and zinc: H. FLASCHKA and F. B. CARLEY, *Talanta*, 1964, **11**, 423. (School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia, U.S.A.)

Summary—Zinc and cadmium can be determined in one solution in the following manner. The sample is adjusted to pH 10 with an ammonia-ammonium chloride buffer so that the total ammonia concentration is 0·02–0·03*M*. Murexide is added so that its amount is in at least 5-fold excess over the amount of zinc present. The titration is performed photometrically at about 450 mμ with ethyleneglycol bis(β-amino-ethylether)-*N,N,N′,N′*-tetra-acetic acid (EGTA) as the titrant. The titration curve obtained shows two breaks which are related to the consecutive titration of cadmium and zinc. The influence of calcium impurities in the reagents used has been studied and a method of pretitration is proposed. For this purpose a small amount of zinc is pretitrated and then the sample solution is added. Thus the calcium blank is established for each titration.

Selective determination of trace amounts of cobalt using the sorption of Co(Phen)$_3^{2+}$ on silica: FRANTIŠEK VYDRA, *Talanta*, 1964, **11**, 433. (Polarographic Institute of the Czechoslovak Academy of Science, Analytical Laboratory, Jilskà 16, Prague, 1, Czechoslovakia.)

Summary—Sorption of Co(Phen)$_3^{2+}$ on silica is not affected by EDTA or citric acid in appropriate conditions of acidity. This fact has been used for the selective determination of microgram amounts of cobalt. Desorption of Co(Phen)$_3^{2+}$ is carried out from an alkaline aqueous-methanolic solution of ammonium formate, and cobalt is determined indirectly, colorimetrically, *via* ferroïn. Special attention has been paid to the determination of trace amounts of cobalt in the presence of iron.

РЕЗЮМЯ

ИССЛЕДОВАНИЕ ХЛОРИСТОВОДОРОДНОГО 2-АМИНО-4-ХЛОРБЕНЗОЛТИОЛА КАК СПЕКТРОФОТОМЕТРИЧЕСКОГО РЕАКТИВА ДЛЯ ОПРЕДЕЛЕНИЯ МОЛИБДЕНА:

G. F. Kirkbright and J. H. Yoe, *Talanta*, 1964, **11**, 415.

Резюме—Хлористоводородный 2-амино-4-хлорбензолтиол творит зеленый осадок с ионами Mo(VI) при pH 2. Осадок можно экстрагировать в хлороформ, максимум абсорбции находится при 720ммк. Чувствительность реакции 0,0054 μг молибдена/см^3 для $\log I_0/I = 0{,}001$. Метод основывается на исследовании эффекта pH, концентрации реактива, скорости комплексообразования и экстракции, температуры и почитании закона Беера. Описанный метод применен для определения молбдена в стали и в чугуне.

ФОТОМЕТРИЧЕСКИЕ ТИТРОВАНИЯ—VII: ПОСЛЕДОВАТЕЛЬНОЕ ТИТРОВАНИЕ КАДМИЯ И ЦИНКА:

H. Flaschka and F. B. Carley, *Talanta*, 1964, **11**, 423.

Резюме—Цинк и кадмий можно определить в одном и том же растворе следующим образом: проба приводится до pH 10 с буферным раствором аммиак—хлорид аммония так, что общая концентрация аммония была бы 0,02—0,03 M. Затем прибавляется мурексид, концентрация которого должна быть в пять раз больше чем концентрация цинка в растворе. Титрование проводится фотометрическим методом при 450 мμ с помощью этиленгликол бис-(-аминоэтил эфир)-N, N, N', N'—тетрауксусной кислоты как титрантом. Полученная крива титрования показывает две инфлексии, которые относятся на последовательное титрование кадмия и цинка. Было исследовано влияние загрязнения кальцием употребленных реактивов и предложен метод предварительного титрования: титруется небольшое количество цинка а затем прибавляется раствор пробы. Этим образом определяется слепая проба кальция для каждого титрования.

ИЗБИРАТЕЛЬНОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ КОБАЛЬТА МЕТОДОМ СОРБЦИИ $Co(Phen)_3^{2+}$ НА СИЛИКАГЕЛЕ:

F. Vydra, *Talanta*, 1964, **11**, 433.

Резюме—ЭДТА и лимонная кислота в подходящей кислотности не мешают сорбции $Co(Phen)_3^{2+}$ на силикагеле. На этом факте основывается метод для избирательного определения кобальта в микрограммовых количествах. Десорбирование $Co(Phen)_3^{2+}$ проводится из щелочного водно-метанолового раствора формиата аммония; кобальт определяется индиректно, колориметрически путем ферроина. Особенное внимание обращается определению следов кобальта в присутствии железа.

The partial separation of mixed solvents in chromatography—I: The selective sorption of liquid media on cellulose and the origin of the second front in paper chromatography: JAN MICHAL and GERHARD ACKERMANN, *Talanta*, 1964, **11**, 441. (Institut für Erzforschung, Praha, ČSSR und Institut für anorganische und analytische Chemie, Bergakademie Freiberg, Sachsen, DDR)

Summary—The course of separation of the components of a solvent mixture by the carrier (cellulose or silica gel) has been investigated. By a study of alcohol-water-acid mixtures it has been shown that in partition chromatography the components of the eluting solvent are partially separated, and that the course of the separation depends on the composition of the original solvent mixture. The hypothesis is proposed that at the boundary between the carrier and the solvent system an intermediate layer forms, in which all the compounds of the solvent are present.

The partial separation of mixed solvents in chromatography—II: Selective sorption of alcohol–water and alcohol–water–acid mixtures on cellulose columns: JAN MICHAL and GERHARD ACKERMANN, *Talanta*, 1964, **11**, 451. (Institut für Erzforschung Praha, ČSSR und Institut für anorganische und analytische Chemie, Bergakademie Freiberg, Sachsen, DDR)

Summary—The character of the selective sorption of alcohol–water and alcohol–water–acid mixtures has been shown to alter on ascending the alcohol series, and with increasing water content. From some mixtures with very low content the alcohol is preferentially sorbed. As the concentration of water increases preferential sorption of water can be shown to occur. For alcohol–water–acid mixtures the acid also participates in the formation of the boundary layer on the cellulose. In the case of air-dried cellulose, it further appears that all the components of the solvent system participate in the formation of the boundary layer between the solid and liquid phases.

РЕЗЫМЯ

ХРОМАТОГРАФИЧЕСКОЕ РАЗДЕЛЕНИЕ РАСТВОРИТЕЛЕЙ I: ИЗБИРАТЕЛЬНАЯ СОРБЦИЯ ЖИДКОСТЕЙ НА ЦЕЛЛЮЛОЗЕ И ПРОИСОЖДЕНИЕ ВТОРОГО ФРОНТА В БУМАЖНОЙ ХРОМАТОГРАФИИ:

J. Michal and G. Ackermann, *Talanta*, **11**, 441.

Резюме—Исследовано разделение компонентов растворителя носителями (целлюлозой, силиконовым гелем). При изучении смесей спирт-вода-кислота, установлено, что в случае частичной хроматографии происходит некоторое разделение элюирующего растворителя. Степень этого разделения зависит от первоначального состава смеси растворителей. Передложена гипотеза, что на поверхности носителя образуется промежуточный слой, в котором присуствуют все компоненты растворителя.

ХРОМАТОГРАФИЧЕСКОЕ РАЗДЕЛЕНИЕ РАСТВОРИТЕЛЕЙ—II: ИЗБИРАТЕЛЬНАЯ СОРБЦИЯ СМЕСЬ СПИРТ-ВОДА И СПИРТ-ВОДА-КИСЛОТА НА КОЛОНКАХ ЦЕЛЛЮЛОЗЫ:

J. Michal and G. Ackermann, *Talanta*, 1964, **11**, 451.

Резюме—Установлено что характер избирательной сорбции из смесей спирт-вода, спирт-вода-кислота меняется в зависимости от повышения содержания воды и в зависимости от положения спирта в гомологическом ряду. Из некоторых смесей с очень низким содержанием воды происходит предпочтительная адсорбция спирта. Можно показать, что предпочтительная сорбция воды происходит с ростом ей концентрации.

Для случая смесей спирт-вода-кислота, обнаружено что кислота тоже может принимать участие в образовании граничащего слоя между твердой и жидкой фазами. Когда применяется целлюлоза высушеная на воздухе все компоненты растворителя принимают участие в формировании граничащего слоя между твердой и жидкой фазами.

Cyanometric titrations in non-aqueous solutions: L. Erdey, O. Gimesi and G. Rády, *Talanta*, 1964, **11**, 461. (Institute of General Chemistry, Technical University, Budapest XI, Gellért tér 4, Hungary.)

Summary—Elemental sulphur can be titrated directly in a benzene-acetone medium with potassium cyanide dissolved in isopropyl alcohol. A potentiometric or visual indicator (bromothymol blue) end-point can be used. Elemental selenium can be determined by dissolving it in an excess of a standard solution of potassium cyanide in isopropyl alcohol and back-titrating the excess with a standard solution of sulphur in benzene-acetone. Selenium and sulphur can also be determined simultaneously. With these titrants, salts of quaternary ammonium bases, dissolved in a mixture of isopropyl alcohol and acetone, can be titrated.

Investigation of reagents for the colorimetric determination of small amounts of cyanide—I: L. S. Bark and H. G. Higson, *Talanta*, 1964, **11**, 471.

Summary—The König synthesis of pyridine dyestuffs by reaction of cyanogen bromide and suitable aromatic amines with pyridine, used as the basis of standard British and American colorimetric methods for the determination of small amounts of cyanide, is reinvestigated. After consideration of the carcinogenic properties of amines capable of being used in a method for cyanide, *p*-phenylenediamine is selected for further examination.

Chelating radiometric titrations by ion exchange for determination of traces of metals: Jiři Starý, Jaromír Růžička and Adolf Zeman, *Talanta*, 1964, **11**, 481. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Praha, 1, Břehová 7, Czechoslovakia.)

Summary—A new type of radiometric titration has been developed. Using EDTA solutions, the negatively charged or neutral metal chelates are formed, and these can easily be separated from the excess of unreacted metal ions using a cation exchanger. Titration curves are constructed from the activities of the eluates. The method has been used for the determination of microgram amounts of indium using ^{114m}In as an isotopic tracer, and for the determination of submicrogram traces of cobalt using the same indicator as a non-isotopic tracer.

РЕЗЮМЯ

ЦИАНОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ В НЕВОДНЫХ РАСТВОРАХ:

L. Erdey, O. Gimesi and G. Rády, *Talanta*, 1964, **11**, 461.

Резюме—Было проведено титрование элементарной серы в среде бензен—ацетон цианистокислым калием, растворенным в изопропиловом спирте. Конец потенциометрического титрования определялся с помощью бромтимолового синего. Стандартное отклонение метода ±0,5%. Элементарный селен определялся с помощью растворения его в избытке стандартного раствора цианистокислого калия, а избыток снова титровался стандартным раствором серы, растворенной в бензен-ацетоновой смеси. Стандартное отклонение метода ±1%. Селен и сера могут быть определены одновременно.

Этими растворами можно титровать соли различных квартерных оснований растворенных в смеси (1:1) пропилового спирта и ацетона. Может употребляться потенциометрическое и визуальное (бромтимоловый синий) определение конца титрования. Стандартное отклонение метода 1%.

ИССЛЕДОВАНИЕ РЕАКТИВОВ ДЛЯ КОЛОРИМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ НЕБОЛЬШИХ КОЛИЧЕСТЬ ЦИАНИДА—I:

L. S. Bark and H. G. Higson, *Talanta*, 1964, **11**, 471.

Резюме—Был пересмотрен синтез Конига красителей образующихся при реакции цианистого брома с соответвующими аминами и служащие стандартами ангдийских и американских колориметрических методов для определения малых количеств цианида. Было исследовано 46 аминов в соответствующих условиях. После исследования карциногенных свойств аминов, которые могли бы быть исcподьзованы, был для далнейшего исследования выбран парафенилендиамин.

КОМПЛЕКСООБРАЗОВАТЕЛЬНАЯ РАДИОМЕТРИЧЕСКАЯ ТИТРАЦИЯ ДЛЯ ОПРЕДЕЛЕНИЯ СЛЕДОВ МЕТАЛЛОВ ИОННЫМ ОБМЕНОМ:

J. Starý, J. Růžička and A. Zeman, *Talanta*, 1964, **11**, 481.

Резюме—Был разработан новый метод радиометрического титрования. Используя раствор ЭДТА, возникают нейтральные или негативно заряженные металические хелаты, которые можно легко разделить от избытка незреагированных металл ионов при помощи катионита. Кривие титрования конструируются из активности элуатов и количества ЭДТА. Метод был применен для определения микрограммовых количеств индия при помощи In^{114} в качестве изотопного индикатора. Методом неизотопного индикатора были определены субмикрограммовые количества кобальта при помощи In^{114}.

Some sulphur-containing organic compounds as reagents for the photometric determination of selenium: A. I. Busev, *Talanta*, 1964, **11**, 485. (M. V. Lomonosov State University, Moscow, U.S.S.R.)

Summary—The reactions of diethylphosphorodithioate, 2-mercaptobenzimidazole, *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine with selenous acid have been studied. Diethylphosphorodithioate and 2-mercaptobenzimidazole react with selenous acid in a 4:1 molar ratio, and with *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine in a 2:1 ratio. New extraction-photometric methods for the determination of small amounts of selenium in various materials not containing tellurium, have been developed, using 2-mercaptobenzimidazole, *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine as reagents.

Anion-exchange behaviour of scandium in chloride-thiocyanate media: H. Hamaguchi, N. Onuma, M. Kishi and R. Kuroda, *Talanta*, 1964, **11**, 495. (Department of Chemistry, Tokyo Kyoiku University, Koishikawa, Tokyo, Japan.)

Summary—A method is described for the separation of scandium from rare earths and thorium by anion exchange. The method utilises the adsorption of a negatively-charged thiocyanato complex of scandium on the strongly-basic anion exchanger Dowex 1-X8 from a $2M$ solution of ammonium thiocyanate in $0{\cdot}5M$ hydrochloric acid. Rare earth elements are not retained on the column, while scandium and thorium show moderate adsorptions and can be separated chromatographically by elution with $3M$ hydrochloric acid. The distribution coefficient data for elements in this medium suggest many possible analytical separations of scandium.

A photometric method for the determination of small amounts of gold with *N*,*N*′-tetramethyl-*o*-tolidine (Tetron): Ch. Daiev and N. Jordanov, *Talanta*, 1964, **11**, 501. (Chemical Faculty, University of Sofia, and Institute for General and Inorganic Chemistry, Bulgarian Academy of Sofia, and Institute of Sciences, Sofia, Bulgaria.)

Summary—A photometric method can be used for the determination of small amounts of gold with *N*,*N*′-tetramethyl-*o*-tolidine (Tetron). The gold is separated by precipitation with tellurium and extraction by ether from an HBr medium, and is then treated with Tetron solution. An orange-yellow colour develops and reaches its full intensity in about 4 min. The solution is diluted, and the colour is measured using a blue filter. The colour is stable for 20–25 min, and then fades gradually. The procedure may be applied to the determination of gold in copper-, lead- and mixed-concentrates or in anode-copper. The results have been evaluated statistically.

РЕЗЮМЯ

НЕКОТОРЫЕ СЕРУСОДЕРЖАЩИЕ ОРГАНИЧЕСКИЕ СОЕДИНЕНИЯ КАК РЕАГЕНТЫ ДЛЯ ФОТОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ СЕЛЕНА:

A. I. Busev, *Talanta*, 1964, **11**, 485.

Резюме—1. Изучено взаимодействие диэтилдитофосфорной кислоты,2-меркаптобензимидазола, N-(меркаптоацетил)-п-анизидина и N-(меркаптоацетил)-п-толуидина с селенистой кислотой. Диэтилдитиофосфорная кислота и 2-меркаптобензимидазол взаимодействуют с селенистой кислотой в молярном отношении 4:1,а N-(меркаптоацетил)-п-анизидин и N-(меркаптоацетил)-п-толуидин в отношении 2:1.

2. Разработаны новые экстракционно-фотометрические методы определения небольших количеств селена в различных объектах, не содержащих теллура, при помощи 2-меркаптобензимидазола, N-(меркаптоацетил)-п-анизидина и N-(меркаптоацетил)-п-толуидина.

АНИОНООБМЕННОЕ ПОВЕДЕНИЕ СКАНДИЯ В СРЕДАХ, СОДЕРЖАЮЩИХ ХЛОРИД—И ТИОЦИАНАТ—ИОНЫ:

H. Hamaguchi, N. Onuma, M. Kishi and R. Kuroda, *Talanta*, 1964, **11**, 495.

Резюме—Опсан метод отделения скандия от редкоземельных элементов и тория при помощи ионообмеников. Метод использует адсорбцию отрицательно заряженого тиоцианатового комплекса скандия на сильно базическом анионите Даузкс 1-Х8 из 2М NH_4SCN в 0,5М HCl растворе. Редкоземельные элементы не задерживаются на колонне, тогда как скандий и торый обнаруживают значительную адсорбцию. Поэтому они могут быть разделены хроматографически с помощью элюции 3М HCl. Коэффициент распределения этих элементов в описанной среде предполагает возможность многих различных аналитических отделений скандия.

ФОТОМЕТРИЧЕСКИЙ МЕТОД ДЛЯ ОПРЕДЕЛЕНИЯ НЕБОЛЬШИХ КОЛИЧЕСТЬ ЗОЛОТА *N,N'*-ТЕТРАМЕТИЛ-*о*-ТОЛИДИНОМ (ТЕТРОНОМ):

Ch. Daiev and N. Jordanov, *Talanta*, 1964, **11**, 501.

Резюме—Небольшие количества золота были определены фотометрически при помощи тетраметил-о-толидина (Тетрона). Золото отделяется соосаждением с теллуром и экстракцией эфиром из среды HBr. Оранжего-желтый цвет соединения золота с Тетроном достигает максимальной интенсивности в течении 4 минут. После разбавления раствора измеряется его светопоглотимость при помощи синего фильтра. Цвет постоянный 20–25 минут. После этого интенсивность постепенно уменьшается. Метод является удобным для определения золота в меди, свинце и смешаных концентратах и продуктах электролиза Резултаты обсуждаются статистическим путем.

Phase titrations—III: New applications, and the phase titration of binary solutions of chemically similar compounds: D. W. Rogers, A. Özsoğomonyan and A. Sümer, *Talanta*, 1964, **11**, 507. (Department of Chemistry, Robert Kolej, Bebek, Istanbul, Turkey.)

Summary—Results are given for the phase titration of 27 new binary solutions of the water-immiscible components dichloromethane, cyclohexane, allyl bromide, benzene, toluene and xylene in combination with the water-miscible components methanol ethanol, isopropanol, dioxan, acetone and acetic acid. A new method for the phase titration of binary solutions of liquids which are chemically similar is described. Results are given for the phase titration of binary solutions of the chemically similar liquids methyl aniline–aniline, nitrobenzene–aniline, carbon tetrachloride–chloroform, n-butyl bromide–n-butyl acetate and cyclohexane–benzene. Sampling procedures and sources of error are discussed.

Enthalpimetric titration of some organic sulphur compounds used in analytical chemistry: E. Popper, L. Roman and P. Marcu, *Talanta*, 1964, **11**, 515. (Department of Analytical Chemistry, Faculty of Pharmacy, Cluj, Rumania.)

Summary—Enthalpimetric titration has been applied to two organic sulphur compounds, 2-mercapto-5-anilino-1,3,4-thiodiazol and hydrazine-*N*,*N*′-bisthiocarbonic acid allyl-monoamide, which are weakly acidic. A discontinuous manual technique has been used, and in the case of the allyl-monoamide a transformation from rectangular to oblique co-ordinates allows for the influence of secondary processes on the thermal effect of the process of neutralisation. From the experimental results the heats of neutralisation of the compounds with sodium hydroxide have also been calculated.

Anion-exchange behaviour of uranium and other elements in the presence of aliphatic di- and tricarboxylic acids: Method for the separation of uranium from thorium and rare earths: J. Korkisch and I. Hazan, *Talanta*, 1964, **11**, 523. (Analytical Institute of the University of Vienna, IX Währingerstrasse 38, Austria.)

Summary—The exchange behaviour of uranium, thorium, the rare earths and some other elements towards the strongly basic anion exchanger Dowex 1 in aqueous and methanolic systems containing di- or tricarboxylic acids is described. Based on the measurement of the distribution coefficients in such media a method for the separation of uranium from thorium and the rare earths in an aqueous solution containing malonic acid has been developed).

РЕЗЮМЯ

ФАЗОВЫЕ ТИТРОВАНИЯ—III. НОВЫЕ ПРИМЕНЕНИЯ И ФАЗОВОЕ ТИТРОВАНИЕ ДВОЙНЫХ РАСТВОРОВ ХИМИЧЕСКИ ПОДОБНЫХ СОЕДИНЕНИЙ:

D. W. ROGERS, A. OSZOGOMONYAN and A. SUMER, *Talanta*, 1964, **11**, 507.

Резюме—Приведены результаты для фазовой титрации для 27 новых двойных растворов не смешивающихся с водой соединений дихлорметана, циклогексана, алилбромида, ензена, толуена, ксилена, в сочетании со смешивающимися с водой соединениями: метанолом, этанолом, изопропанолом, диоксаном, ацетоном и уксусной кислотой. Описан новый метод фазовой титрации бинарных растворов жидкостей химически подобных выше описанным. Приводятся результаты для фазовой титрации двойных растворов химически подобных жидкостей метиланилин-анилин, нитробензен-анилин, тетрахлористый углерод-хлороформ, *n*-бутилбромид-*n*-бутилацетат и циклогексан-бензен. Обсуждается метод подготовки и причины ошибок.

ЭНТАЛЬПИМЕТРИЧЕСКОЕ ТИТРОВАНИЕ НЕКОТОРЫХ ОРГАНИЧЕСКИХ СЕРНЫХ СОЕДИНЕНИЙ, ПРИМЕНЕННЫХ В АНАЛИТИЧЕСКОЙ ХИМИИ:

E. POPPER, L. ROMAN and P. MARCU, *Talanta*, 1964, **11**, 515.

Резюме—Лве слабокислие серосодержащие соединения 2-меркапто-5-анилино-1,3,4,-тиодиазол и гидразин-И,И′-бистиокарбоновая кислота алилмонобромида были определены при помощи энталпиметрической титрации. Применялся ручной перерывный метод. При определении аллил моноамида влияют на температурный эффект нейтрализации тоже вторичные процессы. Из эксперименталных резултатов были вычислены тоже тепла которые выделяются при нейтрализации описаных соединений едким калием.

ИОННООБМЕНЫЕ СВОЙСТВА УРАНА И ДРУГИХ ЭЛЕМЕНТОВ В ПРИСУТСТВИИ АЛИФАТИЧЕСКИХ ДИ- И ТРИКАРБОКСИЛОВЫХ КИСЛОТ:

J. KORKISCH and I. HAZAN, *Talanta*, 1964, **11**, 523.

Резюме—Описано поведение урана, тория и редкоземельных элементов и некоторых других элементов на сильно базическом анионите Дауэкс I в водных и метаноловых системах содержащих ди- и трикарбоновые кислоты. Основывалось на измерениях коэффициента дистрибуции в этих средах. Был разработан метод разделения урана от тория и от редкоземельных элементов в водных растворах, содержащих малоновую кислоту.

Chemical compounds formed in the coprecipitation of cations with sulphides: N. A. Rudnev and G. I. Malofeyeva, *Talanta*, 1964, **11**, 531. (Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, U.S.S.R.)

Summary—A study of the coprecipitation of thallium with As_2S_3, SnS_2, MoS_3, Re_2S_7, PtS_2, PdS, Ru_2S_3, Rh_2S_3, Ir_2S_3 and In_2S_3, and of indium with CuS and Ag_2S by physicochemical analysis has shown that the process results from formation of the following compounds: $TlAsS_2$, $TlSnS_2$, $TlMoS_2$, $TlReS_4$, $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$, $TlRh_2S_4$, Tl_3Ir_3S, $TlIn_2S_3$, $CuInS_2$ and $AgInS_2$. A type of coprecipitation diagram characteristic for the case of the formation of chemical compounds has been established and the fields on it, corresponding to phases of definite composition, have been delimited. The formation in the coprecipitation of microdisperse systems of "colloidal" solid solutions of one sulphide in another has been shown.

A thermogravimetric study of aluminium oxinate: C. J. Keattch, *Talanta*, 1964, **11**, 543. (John Laing Research and Development Ltd., Manor Way, Boreham Wood, Hertfordshire, England.)

Summary—A thermogravimetric study of aluminium oxinate obtained by three different procedures has confirmed the view generally held that 150° is a suitable drying temperature. It has also been shown that this temperature is satisfactory, irrespective of the original moisture content of the precipitate. That a temperature of 700° is sufficient to obtain aluminium oxide is also confirmed. On the other hand, the statement by some workers that aluminium oxinate can be dried at 375° has not been substantiated.

New studies on calcium oxalate monohydrate: A guide to the interpretation of thermogravimetric measurements: E. L. Simons and A. E. Newkirk, *Talanta*, 1964, **11**, 549. (Research Laboratory, General Electric Company, Schenectady, New York, U.S.A.)

Summary—The pyrolysis of calcium oxalate monohydrate in air occupies a unique place in the literature of thermogravimetry. Not only was a thermogram for this reaction the first pyrolysis curve published by Duval and his collaborators, but Duval and others have suggested that it can be used as a reference substance for judging the performance of a thermobalance. However, the pyrolysis of calcium oxalate monohydrate under a variety of conditions gives rise to considerable differences in its thermograms. The effects of sample size, heating rate, atmosphere and container geometry are presented in a series of paired thermograms, and the differences are accounted for with the aid of additional evidence from differential thermal analysis and from combustion train experiments. Variations in atmosphere are particularly important, and the atmospheres studied are dry nitrogen, humidified nitrogen, dry air, humidified air, dry oxygen, dry carbon dioxide and dry carbon monoxide. Even subtle variations in the shape of a thermogram obtained on a reliable balance may reflect the complexity of the reactions that produce the more noticeable over-all weight changes. Results presented in this report thus delineate conditions for the use of calcium oxalate monohydrate as a thermogravimetric reference substance, and show that its behaviour under controlled conditions in a thermobalance can provide an unusually versatile guide to the interpretation of thermogravimetric measurements.

РЕЗЮМЯ

О ХИМИЧЕСКИХ СОЕДИНЕНИЯХ, ОБРАЗУЮЩИХСЯ ПРИ СООСАЖДЕНИИ КАТИОНОВ С СУЛЬФИДАМИ:

N. A. Rudneev and G. I. Malofeyeva, *Talanta*, 1964, **11**, 531.

Резюме—Изучение соосаждения таллия с As_2S_3, SnS_2, MoS_3, Re_2S_7 PtS_2,PdS, Ru_2S_3, Rh_2S_3, Ir_2S_3, In_2S_3 и индия с CuS, Ag_2S методом физико-химического анализа позволило выяснить, что процесс обусловлен образованием соединений: $TlAsS_2$, $TlSn_2S_3$, $TlMoS_2$, $TlReS_4$, $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$, $TlRh_2S_4$, Tl_3Ir_3S, $TlIn_2S_3$, $CuInS_2$ $AgInS_2$. Установлен тип диаграмм соосаждения, характерный для случая образования химических соединений и поля на них, соответствующие фазам определенного состава. Показано образование при соосаждении микродисперсных систем «коллоидных» твердых растворов одного сульфида в другом.

ТЕРМОГРАВИМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ ОКСИНАТА АЛЮМИНИЯ:

C. J. Keattch, *Talanta*, 1964, **11**, 543.

Резюме—Термогравиметрическое изучение оксината алюминия тремя различными методами показало правильность общепринятого взгляда, и именно, что 150°C является подходящей температурой для высушивания. Был также потверден факт, что температура 700°C является достаточной для получения окиси алюминия. Наоборот не было доказано утверждение некоторых авторов, что оксинат алюминия может быть высушен при 375°C.

НОВЫЕ ИССЛЕДОВАНИЯ МОНОГИДРАТА ОКСАЛАТА КАЛЬЦИЯ: УКАЗАТЕЛЬ ДЛЯ ИНТЕРПРЕТАЦИИ ТЕРМОГРАВИМЕТРИЧЕСКИХ ДАННЫХ:

E. L. Simons and A. E. Newkirk, *Talanta*, 1964, **11**, 549.

Резюме—Пиролиз моногидрата оксалата кальция в воздухе занимает особенное место в литературе по термогравиметрии. Не только термограмма этой реакции была первая крива пиролиза опубликована Дювалом и сотрудниками, но Лювал и другие тоже предлагали это соединение как эталон для оценки термовесов. Между тем, термограммы очень различны если пиролиз моногидрата оксалата кальция проводится в различных условиях. В ряде парных термограмм приказан эффект количества пробы скорости нагревания, атмосферы, геометрии сосуда. Разницы обсняются помощью дополнительных данных, полученных диференциальным термическим анализом и опытами на установке для злементарного анализа. Весьма важны колебания атмосферы: опыты проведены в сухом азоте, влажном азоте, сухом воздухе, влажном воздухе, сухом кислороде, сухом двуокисе углерода и сухом окисе углерода. Даже незначительние колебания в форме термограммы, полученой на совсем надежных весах, могут отражать сложность реакций которые производят более приметные общие перемены веса. Результаты приведенные в этой статье ограничивают таким образом условия для пользования моногидрата оксалата кальция как термогравиметического эталона и показывают что это соединение при определенных условиях может послужить как весьма многосторонный указатель для интерпретации термогравиметрических измерений.

Colorimetric determination of nickel with 2-mercaptobenzothiazole: E. G. Walliczek, *Talanta*, 1964, **11**, 573. (Rhoanglo Mine Services Ltd., Research and Development Division, P.O. Box No. 172, Kitwe, N. Rhodesia.)

Summary—A colorimetric method has been developed for determining nickel with 2-mercaptobenzothiazole. At pH 7·7–8·1 in an ammoniacal medium nickel forms a yellow-brown complex, insoluble in water but soluble in chloroform. It is suitable for determining nickel in the concentration range 0·4–16 ppm with an average error of 0·5–2%. Cobalt, copper and iron interfere and have to be removed by an anion-exchange method before analysis. Bismuth and lead, if present, are removed with hydrogen sulphide, and complex formation of 2-mercaptobenzothiazole with alkali metals is prevented by fluoridation. No other metals were found to interfere.

Determination of gases in metals by an improved vacuum fusion technique: T. Somiya, S. Hirano, H. Kamada and I. Ogahara, *Talanta*, 1964, **11**, 581. (Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, 1, Hongo-Motofuji, Tokyo, Japan.)

Summary—An improved gas extraction, collection, pressure measurement and calculation apparatus is described for use in the vacuum fusion method. It is designed for routine analysis and versatility in research investigations. The time required for gas collection is 1–2 min, including 15–60 sec for gas extraction. The total time required for a complete analysis is 7–9 min. The operating blank is 0·01–0·03 ml/30 min at 1850°. Analysis of 20 or more samples can be made in 8 hr, including loading, outgassing and gas analysis. A description is given of a newly designed gas extraction recording system for studying the optimum conditions for determination of gases in metals of current interest.

Pioneers of electroanalysis: F. Szabadváry, *Talanta*, 1964, **11**, 593. (Institut für allgemeine Chemie, Technische Universität, Budapest, Ungarn.)

Summary—The pioneers and the most outstanding research workers in the different branches of electro-analysis—electrodeposition, pH measurement, potentiometric and conductometric titration, coulometry, polarography and amperometry, and the inventors of the commoner types of electrodes are discussed. Brief biographies are given for most of the individuals mentioned.

Liquid-liquid extraction of tungsten^{VI} with tributyl phosphate: Anil K. De and M. Syedur Rahaman, *Talanta*, 1964, **11**, 601. (Department of Chemistry, Jadavpur University, Calcutta, 32, India.)

Summary—A new method has been developed for the rapid extraction of tungsten^{VI} with tributyl phosphate (TBP). Quantitative extraction occurs from 8–10M hydrochloric acid using 100% TBP. Tungsten is finally determined spectrophotometrically as thiocyanate. The extractable species is probably $WO_2Cl_2.2TBP$. There are very few interferences. The method is shown to be applicable to an alloy steel.

КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИКЕЛЯ 2-МЕРКАПТОБЕНЗТИАЗОЛОМ:

E. G. WALLICZEK, *Talanta*, 1964, **11**, 573.

Резюме—Был разработан количественный колориметрический метод для определения никеля 2-меркаптобензтиазолом. Никель образует в аммиачновой среде (pH 7,7 8,1) желтокоричневый комплекс, нерастворимый в воде но растворимый в хлороформе, который можно использовать для определения никеля в концентрациях от 0,4 до 16 частиц/миллион со средней ошибкой 0,5–2%. Кобальт, медь и железо, которые мешают определению нужно устранить при помощи анионного обмена. Если присутствуют Bi и Cu нужно их удалить при помощи сероводорода. В работе тоже учитывается влияние щелочных металлов. Другие металлы не мешают определению.

ОПРЕЛЕЛЕНИЕ ГАЗОВ В МЕТАЛЛАХ УЛУЧШЕННЫМ МЕТОДОМ ПЛАВЛЕНИЯ В ВАКУУМЕ:

T. SOMIYA, S. HIRANO, H. KAMADA and I. OGAHARA, *Talanta*, 1964, **11**, 581.

Резюме—Описывается улучшенный аппарат для экстрагирования и сбора газов, измерения давления и вычисления результатов, которым пользуется метод плавления в вакууме. Аппарат устроен для рутинного анализа и многосторонного применения в научных исследованиях. Сбор газов окончен после 1–2 мин., включая их экстрагирование (15–60 сек.). Продолжительность полного анализа 7–9 мин. Слепой отсчет 0,01–0,03 мл./30 мин. при 1850°. В течении 8 часов можно анализировть 20 или больше проб, включая загрузку, дегазирование и анализ газа. Описывается новая конструкция самопишущей систем дегазации, которая особенно подходящая для определения оптимальных условий анализа газов в металлах.

ПИОНЕРЫ ЭЛЕКТРОАНАЛИЗА:

F. SZABADVARY, *Talanta*, 1964, **11**, 593.

Резюме—Дискутируется участвие различных ученых в развитии областей электроанализа—в особености это электролиз, измерение pH, потенциометрические и кулонометрические титрации, кондуктометрические титрование, поляроərафия и амперометрия. В работе описаны тоже биографии большинства вышеупомянутых лиц.

Liquid-liquid extraction of tungsten with tributyl phosphate: ANIL K. DE and M. SYEDUR RAHAMAN, *Talanta*, 1964, **11**, 601.

Резюме—Разработан новый быстрый метод экстрагирования трибутилфосфатом/ТБФ/. Экстракция количественная из среды 8–10M HCl при помощи 100% ТБФ. Вольфрам определяется спектрофотометрически в виде тиоцианата. Вероятный состав экстрагируемого вещества WO_2Cl_2 2 TBF. Определению мешает только небольшое количество веществ. Метод можно использовать для анализа сталей.

Indirect determination of traces of uranium using 1-(2-pyridylazo)-2-naphthol: M. R. Hayes and J. S. Wright, *Talanta*, 1964, **11**, 607. (United Kingdom Atomic Energy Authority, Springfields Works, Salwick, Preston, Lancashire, England.)

Summary—In the determination of traces of uranium using 1-(2-pyridylazo)-2-naphthol (PAN), solvent extraction of the complex is replaced by the separation of the insoluble complex from homogeneous solution. This is followed by hydrolysis to give free PAN equivalent to the uranium present. An increase in sensitivity of almost 50% results, and the conditions for complex formation require less stringent control. A general method for the determination of uranium in impure liquors is described. Reversed-phase partition chromatography is used for the initial separation of uranium, followed by the use of complexing agents to prevent interference from any residual ions. The method is simple and rapid, and the precision compares favourably with other methods using PAN.

Application of cationic-sensitive glass electrodes to the study of alkali metal complexes—I: The sodium-malate system: G. A. Rechnitz and J. Brauner, *Talanta*, 1964, **11**, 617. (Department of Chemistry, University of Pennsylvania, Philadelphia 4, Pennsylvania, U.S.A.)

Summary—Cationic-sensitive glass electrodes are used to study the weak complex formed by sodium ion and malic acid in aqueous media. The best value of 1·1 ± 0·3 for the calculated formation constant agrees well with literature values. Methods of measurements and calculation are described and evaluated.

Investigation of reagents for the colorimetric determination of small amounts of cyanide—II: A proposed method for trace cyanide in waters: L. S. Bark and H. G. Higson, *Talanta*, 1964, **11**, 621. (Department of Chemistry and Applied Chemistry, Royal College of Advanced Technology, Salford 5, Lancashire, England.

Summary—*p*-Phenylenediamine is used in a König-type reaction for the determination of trace amounts of cyanide in waters. With slight variation in procedure, the method is applicable over the range 0·005–100 ppm.

Wet oxidation of organic compositions: Mixed nitric and hydrochloric acids with ammonium perchlorate as oxygen donors: G. Frederick Smith, *Talanta*, 1964, **11**, 633. (Noyes Chemical Laboratories, University of Illinois, Urbana, Illinois, U.S.A.)

Summary—The wet oxidation of organic compositions as introductory manipulation in the determination of micro- and macrogram metallic and non-metallic elements is described. The principal oxygen donor in this procedure is perchloric acid generated *in situ*. Mixed nitric and hydrochloric acids are employed to convert ammonium perchlorate to perchloric acid. The three mixed acids then serve as superior solvent for the organic matter to be oxidised. Conditions are particularly suited for the oxidation of large samples. Reaction rates are repressively controlled to give assurance against violent oxidation. Applications include organic compositions, essentially of cellulose, sugars and polyhydric alcohols, or proteins. Conditions prevail in the leisurely application of reaction time to provide maximum effects from nitric acid. This provision is the key to slowly advancing oxidation potential. The final high potential provided by perchloric acid over the temperature range 150° to 203°, stepwise increasing, completes oxidations with no accompanying menacing carbonisations. Reaction times involve 50 to 60-min digestions.

РЕЗЮМЯ

КОСВЕННОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ УРАНА ПРИ ПОМОЩИ 1-(2-ПЫРИДИЛАЗО)-2-НАФТОЛА:

M. R. Hayes and J. S. Wright, *Talanta*, 1964, **11**, 607.

Резюме—При определении следов урана при помощи ПАН, метод экстракции замещается осаждением нерастворимого комплекса мз гомогенного раствора. Потом гидролизом освобождается эквивалентное содержанию количество ПАН.

Описан метод для определения урана в жидкостях. Уран отдаляется от мешающих элементов при помощи распределительной хроматографии; остаточные ионны маскируются при помощи комплексирующих веществ. Метов является простым, быстрым и его точность лучше чем остальных методов использующих ПАН.

ПРИМЕНЕНИЕ КАТИОНОЧУВСТВИТЕЛЬНЫХ СТЕКЛЯННЫХ ЭЛЕКТРОДОВ В ИССЛЕДОВАНИИ КОМПЛЕКСОВ ЩЕЛОЧНЫХ МЕТАЛЛОВ-I: СИСТЕМА НАТРИЙ-МАЛАТ:

G. A. Rechnitz and J. Brauner, *Talanta*, 1964, **11**, 617.

Резюме—Для изучения слабого комплекса иона натрия с малеиновой киспотой в водном растворе был использован стеклянный электрод чувствительный на катионы. Лучше значение константы образования (1,1 ± 0,3) хорошо совпадает с литературными данными. Были разработаны и описаны методы измерения и вычислений.

МЕТОД ДЛЯ КОЛОРИМЕТИЧЕСКОГО ОПРЕДЕЛЕНИЯ СЛЕДОВЫХ КОЛИЧЕСТВ ЦИАНИД-ИОНА В ВОДАХ:

L. S. Bark and H. G. Higson, *Talanta*, 1964, **11**, 621.

Резюме—Описывается определение следовых количеств цианид-иона в водах п-фенилендиамином, в реакции типа Кенига.С небольшим изменением процедуры, метод может применяться в области 0,005–100 мг/л.

МОКРОЕ ОКИСЛЕНИЕ ОРГАНИЧЕСКИХ ВЕЩЕСТВ. СМЕСЫ АЗОТНОЙ И СОЛЯНОЙ КИСЛОТ С ПЕРХЛОРАТОМ АММОНИЯ КАК ПОДАТЕЛЕМ КИСЛОРОДА:

G. F. Smith, *Talanta*, 1964, **11**, 633.

Резюме—Описано мокрое окисление органических веществ как предварительная операция при определении металлов и металлоидов в миро- и макро-анализе. Главный податель кислорода в этом методе есть образована "In situ" хлорная кислота. Смесы азотной и соляной кислот служат для превращения перхлората аммония в хлорную кислоту. Смесь этих трех кислотслужит затем, как замечательный растворитель для окисляемого органического вещества. Лучше всего окисляются большие пробы.

Скорость реакции регулирована, чтобы избеч сильное окисление. Метод главным образом применен на целлюлозу, сахары и многоатомные спирты или белки. Время реакции продолжается чтобы азотная кислота могла дать максимальный эффект. В этом ключ к постепенно растущем потенциале окисления. Конечный высокий потенциал вызван хлорной кислотой в области температуры 150–203°C растет постепенно и оканчивает окисления без сопровождающих карбонизаций. Реакция окончена после 50–60 мин.

5-(8-Hydroxy-5-quinolylmethyl)-8-hydroxy-1-methylquinolinium salts as solvatochromic chelating agents: J. W. Faller and J. P. Phillips, *Talanta*, 1964, **11,** 641. (Department of Chemistry, University of Louisville, Louisville, Kentucky, U.S.A.)

Summary—The title compounds and related substances were prepared, characterised and tested as solvatochromic chelating agents. These reagents show large colour changes with solvent, and the chelates, though insoluble in most common solvents, are also solvatochromic. Reagents with a 2-methyl group adjacent to the chelating centre do not precipitate aluminium, and this effect can be used as a colour test for aluminium.

Bisbiacetylmonoxime-ethylenedi-imine and bisbiacetylmonoxime-*o*-phenylenedi-imine as new gravimetric reagents for nickel and palladium: N. K. Mathur and C. K. Narang, *Talanta*, 1964, **11,** 647. (Department of Chemistry, M.B.M. Engineering College, University of Jodhpur, Jodhpur, India.)

Summary—The condensation products of diketone monoximes with diamines have been shown to form precipitates with nickel which contain metal and reagent in the ratio 1:1, and can be used for the gravimetric determination of nickel.

Amperometric determination of lanthanum as molybdate: R. S. Saxena and M. L. Mittal, *Talanta*, 1964, **11,** 649. (Chemical Laboratories, Government College, Kota, Rajasthan, India.)

Summary—The reaction between lanthanum and molybdate ions has been followed by means of direct and reverse amperometric titration in aqueous and aqueous-alcoholic media at an applied potential of $-1\cdot5$ V (*vs.* S.C.E.). The amperometric end-point obtained from the sharp break in the titration curves occurs when the molecular ratio of $La^{3+}:MoO_4^{2-}$ is 2:3 and corresponds to the formation and precipitation of normal lanthanum molybdate, $La_2O_3.3MoO_3$, at pH 5–6. Amperometric titrations yield very accurate and reproducible results and offer a simple and rapid method for the determination of lanthanum as molybdate even at low concentrations ($1 \times 10^{-3}M$ lanthanum nitrate).

Phase titrations—IV: New applications including the assay of water in pyridine: D. W. Rogers and A. Özsoğomonyan, *Talanta*, 1963, **10,** 652. (Chemistry Department, Robert Kolej, Bebek, Istanbul, Turkey.)

Summary—The assay of water in organic solvents by means of phase titration has been discussed in relation to the chloranilic acid method of Barreto and Barreto (*Analyt. Chim. Acta*, 1962, **26,** 494) and the older cloud-point technique. Results are given for the titration of water-pyridine solutions with chloroform, as representative of the phase titration of a nitrogen-containing compound to which the chloranilic acid method is inapplicable. In addition, results are given for the phase titration of 18 new binary solutions using water as the titrant. They are bromobenzene, chloroform and 1,2-dibromoethane, each in binary solution with methanol, ethanol, isopropanol, dioxan, acetone and acetic acid.

РЕЗЮМЯ

СОЛИ 5-(8-ХИДРОКСИ-5-ХИНОЛИЛМЕТИЛ)-8-ХИДРОКСИ-1-МЕТИЛ-ХИНОЛИНИЯ КАК СОЛЬВАТОХРОМНЫЕ ХЕЛАТООБРАЗНЫЕ АГЕНТЫ:

J. W. Faller, and J. P. Phillips, *Talanta*, 1964, **11**, 641.

Резюме—Соединение в заглавии и сродные вещества были произведены, характеризованы и испытаны как сольватохромные хелатообразные агенты. Эти реагенты показывают резкие перемены окраски в зависимости от растворителя; хелаты, хотя не растворимы в большинстве обыкновенных растворителях, тоже сольватохромы. Реагенты, у которых 2-метил группа соседная хелатообразном центре, не осаждают алюминий; этим эффектом можно пользоваться как цветной реакцией для алюминия.

БИС-ДИАЦЕТИЛМОНОКСИМ-ЭТИЛЕНДИИМИН И БИС-ДИАЦЕТИЛМОНОКСИМ-О-ФЕНИЛЕНДИИМИН-НОВЫЕ РЕАГЕНТЫ ДЛЯ ВЕСОВОГО АНАЛИЗА НИКЕЛЯ И ПАЛЛАДИЯ:

N. K. Mathur and C. K. Narang, *Talanta*, 1964, **11**, 647.

Резюме—Продукты конденсации дикетоновых моноксимов с диаминами образуют осадки с никелем, которые содержат металл и реагент в отношении 1:1. Они могут послужить для весового определения никеля.

АМПЕРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЛАНТАМА В ФОРМЕ МОЛИБДАТА:

R. S. Saxena and M. L. Mittal, *Talanta*, 1964, **11**, 649.

Резюме—Реакция между ионами лантана и молибдата была исследована с помощью прямого и обратного амперометрического титрования в водных и аводно-спиртовых средах при потенциале −1,5 V (в отношении к стандартном каломелььевом электроде). Амперометрический конец титрования, приказан острой инфлексией в криве титрования, обнаруживается когда молекулярное отношение $La^{3+}:MoO_4^{2-}$ равно 2:3. Он совпадает с образованием и осаждением нормального молибдата лантана, $La_2O_3.3MoO_3$, при pH 5–6. Амперометрическим титрованием получаются весьма точные и воспроизводимые результаты; это простой и быстрый метод для определения лантана в форме молибдата, даже при низких концентрациях (1×10^{-3}M нитрата лантана).

ФАЗОВОЕ ТИТРОВАНИЕ—IV: НОВЫЕ ПРИМЕНЕНИЯ МЕТОДА, ВКЛЮЧАЯ ОПРЕДЕЛЕНИЕ ВОДЫ В ПИРИДИНЕ:

D. W. Rogers and A. Özsoǧomonyan, *Talanta*, 1964, **11**, 652.

Резюме—Анализ воды в органических растворителях помощью фазового титрования рассматривается в сравнении с методом хлораниловой кислоты Баррето и Баррето (*Analyt. Chim. Acta*, 1962, **26**, 494) и со старшим методом, пользующимся точкой помутнения. Приводятся результаты титрования хлороформом растворов воды в пиридине; это случай фазового титрования одного соединения содержающего азот, где не может быть применен метод хлораниловой кислоты. Кроме того сообщены результаты фазового титрования 18 новых двойных растворов, пользуясь водой как титрантом. Это бромбензол, хлороформ и 1,2-дибромэтан, каждый из них в двойном растворе с метиловым, этиловым и изопропиловым спиртами, диоксаном, ацетоном и уксусной кислотой.

A simple method for the determination of carbon in uranium and plutonium carbides: H. D. Sharma and M. S. Subramanian, *Talanta*, 1964, **11,** 655. (Radiochemistry and Isotope Division, Atomic Energy Establishment Trombay, Bombay, India.)

Summary—A simple method for the determination of combined and free carbon in the carbides of uranium and plutonium is based on the examination of the oxidation of carbide and free carbon thermogravimetrically. The combined carbon (carbide) oxidises to carbon dioxide in air below 500° while the free carbon oxidises above 600°. This allows the determination of both combined and free carbon in a single sample, using a furnace tube and a conventional method for carbon dioxide.

Possibility of automation of potentiometric EDTA titrations: R. C. Schonebaum and E. Breekland, *Talanta*, 1964, **11,** 659. (Koninklijke/Shell-Laboratorium, Amsterdam, Badhuisweg 3, Amsterdam-N, Netherlands.)

Summary—Experiments are described which show that many metals can be determined in a simple way with the aid of the Beckman model K automatic titrator. As regards accuracy, the method is in many cases practically on a par with manual titrations.

An investigation of the Gibbs colour reaction of phenol: F. Feigl, V. Anger and H. Mittermann, *Talanta*, 1964, **11,** 662 (Chemical Laboratory, Vienna XVIII/110, Teschner 35, Austria.)

Summary—The influence of substituents on the reactivity of phenols towards 2,6-dibromoquinone-4-chlorimine and its chloro analogue has been investigated. It has been shown that substituents in the *m*-position have little influence, whereas *o*-substituents with a C=O or N=O group prevent the reaction taking place.

РЕЗЮМЯ

ПРОСТОЙ МЕТОД ДЛЯ ОПРЕДЕЛЕНИЯ УГЛЕРОДА В КАРБИДАХ УРАНА И ПЛУТОНИЯ:

H. D. Sharma and M. S. Subramanian, *Talanta*, 1964, **11**, 655.

Резюме—Описан простой метод для определения связанного и свободного углерода в карбидах урана и плутония, основан на определении окисления карбида и свободного углерода термогравиметрическим методом. Связанный углерод (карбиды) окисляется в двуокись углерода в воздухе ниже 500°C, пока свободный углерод окисляется выше 600°C. Это позволяет определение в одной и той же пробе, как связанного, так и свободного углерода с помощью трубчатой печи и обыкновенного метода для определения двуокиси углерода. Стандартная ошибка при определении связанного и свободного углерода показалась 1,6% и 3,2% в случае карбидов урана и соответственно 0,3% и 3,9% в случае карбидов плутония.

НЕКОТОРЫЕ НАДЕЖНЫЕ ВОЗМОЖНОСТИ НОТЕНЦИОМЕТРИЧЕСКИХ ТИТРАЦИЙ С ИСПОЛЬЗОВАНИЕМ ЭДТА. II. БОЗМОЖНОСТЬ АВТОМАТИЗАЦИИ:

R. C. Schonebaum and E. Breekland, *Talanta*, 1964, **11**, 659.

Резюме—Опсаны опиты из которых следует что многие металлы можно несложно определить при помощи титратора типа Бэкман-К. Точность определения сравнивается с титацией при помощи ручного управления.

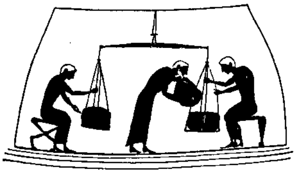
ИССЛЕДОВАНИЕ ЦВЕТНОЙ РЕАКЦИИ ГИББСА ДЛЯ ФЕНОЛОВ:

F. Feigl, V. Anger and H. Mitterman, *Talanta*, 1964, **11**, 662.

Резюме—Испитано влияние заместителей на реактивность фенола к 2,6-дибромхинон-4-хлоримину и его хлор-аналоге. Показано что заместители в мета-положении не имеют большое влияние, но заместители в орто-положении которые содержат группы C=O или И=O предовращают реакцию.

TALANTA

An International Journal of Analytical Chemistry



EDITOR-IN-CHIEF

Professor Cecil L. Wilson, Department of Chemistry, The Queen's University, Belfast, Northern Ireland

ASSOCIATE EDITOR

Dr. M. Williams, Department of Chemistry, College of Advanced Technology
Gosta Green, Birmingham, 4, England

ASSISTANT EDITOR

Dr. D. Betteridge, Department of Chemistry, University College of Swansea, Wales

REGIONAL EDITORS

Professor I. P. Alimarin, Vernadsky Institute of Geochemistry and
Analytical Chemistry, Academy of Sciences,
Vorobievskoe Shosse 47a, Moscow V-334, U.S.S.R.

Professor L. Gordon, Department of Chemistry, Case Institute of Technology
Cleveland, 6, Ohio, U.S.A.

Dr. R. Přibil, Laboratory of Analytical Chemistry, Polarographic Institute, Czechoslovak Academy
of Sciences, Praha, 1, Jilská 16, Czechoslovakia

Professor G. Gopala Rao, Department of Chemistry, Andhra University
Waltair, S. India

Professor T. Takahashi, Institute of Industrial Science, University of Tokyo, Japan

EDITORIAL BOARD

Chairman: Mr. Robert Maxwell, *Chairman and Managing Director, Pergamon Press Ltd.*
Professor C. L. Wilson, *Editor-in-Chief* Dr. M. Williams, *Associate Editor*
Dr. D. Betteridge, *Assistant Editor*
Professor L. Gordon, *representing Regional Editors*
Professor R. Belcher, *representing Advisory Board*
Mr. G. F. Richards, *Joint General Manager, Pergamon Press Ltd.*

PERGAMON PRESS LTD.

4 & 5 FITZROY SQUARE, LONDON W.1 122 EAST 55TH STREET, NEW YORK 22, N.Y.

Publishing Offices: Headington Hill Hall, Oxford (Oxford 64881).

Published monthly - 1 Volume *per annum*

Annual subscription (including postage): (A) for Libraries, Government Establishments and Research Institutions—£26 ($75). (B) for private individuals, who place their orders with the Publisher and who certify that the Journal is for their personal use—£5.5. ($15).

(C) for *bona fide* students—£3.10. ($10).

Payments must be made in advance

Copyright © 1964

Pergamon Press Ltd.

The illustration of a Greek balance from one of the Hope Vases is reproduced here by kind permission of Cambridge University Press

PRINTED IN NORTHERN IRELAND AT THE UNIVERSITIES PRESS, BELFAST

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable. Original papers, preliminary and short communications, reviews and letters will be published.

Because TALANTA is an international journal, contributions are expected to be of a very high standard. They should make a definite contribution to the subject. Papers submitted for publication should be new publications. The submission of a paper is held to imply that it has not previously been published **in any language,** that it is not under consideration for publication elsewhere, and that, if accepted for publication, it will not be published elsewhere without the written consent of the Editor-in-Chief. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, **but should be critical.** The Editor-in-Chief will welcome correspondence on matters of interest to analytical chemists.

Original papers, short communications and reviews will be refereed (see *Talanta*, 1962, **9**, 89). Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor-in-Chief, the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

Preliminary communications will be refereed urgently, and will be accorded priority in publication. Letters to the Editor will not be refereed, but will be published at the discretion of the Editor-in-Chief. If accepted, they will also be given priority.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

General

Contributions should be submitted to the Editor-in-Chief, **or to the appropriate Regional Editor,** and may be written in English, German or French.

Preliminary communications should be limited to less than 1000 words in length and should not contain diagrams. If they do not fulfill these conditions they will be treated as short communications.

Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced. Where possible, papers should follow the pattern: *Introduction, Discussion, Conclusion, Experimental* (or such of these headings as apply).

Because all material will be set directly in page proof, every attempt should be made to ensure that before being submitted, manuscripts are essentially in the final form desired by the authors, and that no alterations of moment will be required at the proof stage. Alterations suggested by the referee will be agreed with the authors at the manuscript stage. Authors whose native language is not English are advised that in submitting papers in English they should endeavour to have the paper thoroughly corrected before submitting for publication. If the manuscript requires considerable editing, it may have to be returned to the authors for retyping, resulting in a serious delay in publication.

Summaries

The essential contents of each paper should be briefly recapitulated in a summary placed at the beginning of a paper, or at the end of a preliminary or short communication. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

Illustrations

Illustrations should be separate from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. **If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; this will ensure more rapid publication. It is**

not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, because they are easily available to the printers:

△ △ ⊡ □ ● **○** ◬ ⊙ ⊕ ⊖ ⏻ ⊗

Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, *e.g.*, standard deviation. The same information should not be produced in both tables and figures.

The preferred positions for all figures and tables should be indicated in the manuscript by the authors.

References

References should be indicated in the text by consecutive superior numbers; and the full reference should be given in a list at the end of the paper in the following form:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, 57, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶. commencing anew on each page; they should not be included in the numbered reference system.

Proofs

Proofs will be sent out to authors in page form for correction. **It is emphasised that at this stage extensive alterations to the text or failure to return the corrected proofs promptly may result in serious delay in publication.**

Authors are particularly requested to check the correctness of their references, which should, at some stage, also be checked against the original papers.

Miscellaneous

Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units. In editing papers for publication the conventions used, on the whole, will be English spelling for all matter in the English language, and the general usages described in *Handbook for Chemical Society Authors* (The Chemical Society, London, Special Publication No. 14, 1960). It would be helpful if authors would consult this for guidance in the preparation of their manuscripts. Authors who wish to retain American spelling, or to adhere to other generally accepted usages, should indicate this clearly at the time of submission of the manuscript.

Where several authors are involved in a paper, an indication of the author to whom requests for reprints should be addressed may be given by placing the symbol ® after the name of that author.

By following the Script Requirements carefully, authors will assist greatly in ensuring rapid publication.

ADVISORY BOARD

Chairman: Professor R. Belcher	University of Birmingham, England
Professor G. Ackermann	School of Mines, Freiberg, German Democratic Republic
Dr. D. M. W. Anderson	University of Edinburgh, Scotland
Professor F. E. Beamish	University of Toronto, Ontario, Canada
Mr. E. Bishop	University of Exeter, England
Professor A. I. Busev	M. V. Lomonosov State University, Moscow, U.S.S.R.
Dr. E. A. M. F. Dahmen	Koninklijke/Shell Lab., Amsterdam, Netherlands
Professor L. Erdey	Technical University, Budapest, Hungary
Professor Fritz Feigl	Ministry of Agriculture, Rio de Janeiro, Brazil
Professor H. Flaschka	Georgia Institute of Technology, Atlanta, Georgia, U.S.A.
Mr. J. K. Foreman	U.K.A.E.A., Windscale Works, Cumberland, England
Professor H. Freiser	University of Arizona, Tucson, Arizona, U.S.A.
Professor R. B. Hahn	Wayne State University, Detroit, Michigan, U.S.A.
Mr. J. O. Hibbits	General Electric Company, Cincinnati, Ohio, U.S.A.
Professor K. J. Karrman	University of Lund, Sweden
Professor W. Kemula	University of Warsaw, Poland
Professor G. Kortüm	University of Tübingen, German Federal Republic
Professor Shu-Chuan Liang	Academia Sinica, Peking, China
Dr. R. J. Magee	The Queen's University, Belfast, Northern Ireland
Professor H. Malissa	Technical University, Vienna, Austria
Professor J. Minczewski	Politechnika Warsaw, Poland
Mr. John Mitchell, Jr.	E. I. duPont de Nemours, Wilmington, Delaware, U.S.A.
Dr. D. F. C. Morris	Brunel College, London, England
Dr. Maurice Pesez	Roussel-Uclaf, Paris, France
Dr. G. A. Rechnitz	University of Pennsylvania, Philadelphia, U.S.A.
Professor W. Rieman III	Rutgers University, New Brunswick, U.S.A.
Professor L. B. Rogers	Purdue University, Lafayette, Indiana, U.S.A.
Professor E. Schulek	L. Eötvös University, Budapest, Hungary
Professor G. Frederick Smith	University of Illinois, Urbana, Illinois, U.S.A.
Dr. M. Steinberg	The Hebrew University of Jerusalem, Israel
Professor E. H. Swift	California Institute of Technology, Pasadena, California, U.S.A.
Professor N. Tanaka	Tohoku University, Sendai, Japan
Dr. E. Wänninen	Åbo Academy, Finland
Dr. T. S. West	Imperial College, University of London, England
Dr. D. H. Wilkins	General Electric Company, Schenectady, U.S.A.
Professor Hobart H. Willard	University of Michigan, Ann Arbor, Michigan, U.S.A.
Mr. A. F. Williams	I.C.I., Ltd., Nobel Division, Stevenston, Scotland
Mr. D. W. Wilson	Sir John Cass College, London, England
Dr. P. Zuman	Polarographic Institute, Czechoslovak Academy of Science, Prague, Czechoslovakia

Talanta, 1964, Vol. 11, pp. 385 to 392. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF THE OXIDATION STATES OF TRACER URANIUM, NEPTUNIUM AND PLUTONIUM IN AQUEOUS MEDIA

S. C. Foti and E. C. Freiling
U.S. Naval Radiological Defense Laboratory, Chemical Technology
Division, San Francisco, Calfornia, U.S.A.

(*Received* 8 *January* 1962. *Revised* 23 *July* 1963. *Accepted* 10 *August* 1963)

Summary—This report describes the development, testing and application of a chemical procedure for determining the distributions of uranium, neptunium and plutonium among their respective oxidation states in various aqueous media at tracer concentrations. The separations achieved are of the order of 95% clean. Results are presented which show the per cent extraction of uranium, neptunium and plutonium oxidation states by 0·4*M* 2-thenoyltrifluoracetone at various values of pH, and per cent carried by lanthanum fluoride from distilled water and sea water under various conditions. Radiochemical analysis of the separated fractions can then be used to determine the required oxidation state distributions.

INTRODUCTION

Uranium, neptunium and plutonium oxidation state determinations become increasingly important as the utilisation of nuclear power expands, the study of radioactive fallout progresses, and plans are made to test peaceful applications of nuclear explosions. Published material provides much useful information, but some of this is conflicting, and additional data are required to permit reliable measurements of oxidation state distributions. This report describes the development and testing of a method for determining the distribution of tracer concentrations of uranium, neptunium and plutonium among their respective oxidation states in aqueous media. Some areas of application are as follows.

The contribution of uranium-237 and neptunium-239 to the gross activity after a nuclear detonation may be appreciable for a period of ten half lives for each radionuclide.[1] Nuclear detonations in sea water will cause significant quantities of these radionuclides to be present in the aqueous phase of the debris.[2] Nuclear reactor accidents at sea or in the air above are more recent potential sources of sea water contamination by these nuclides as well as by plutonium-239. The biological fate of such contaminants would be expected to depend upon their oxidation states.

The chemical behaviour of uranium, neptunium and plutonium in the process of concentrating, isolating and purifying these elements from aqueous solutions will depend upon their oxidation states. It is therefore important to have means of verifying predicted species.

The development of an oxidation state separation scheme at the tracer level is beset with certain inherent difficulties. The only observable properties of a tracer which give evidence of the oxidation state arise from its chemical behaviour, which in most instances closely resembles the chemical behaviour of the element at macro concentrations. However, the importance of such effects as radiocolloid formation, adsorption on container walls, and oxidation state perturbation by small amounts of impurities becomes greatly magnified at tracer levels, and modifies the properties observed. Two other peculiarities of tracer behaviour are particularly appropriate. The first involves the kinetics of homogeneous bimolecular reactions when both reactants are present at tracer concentrations. Such reactions include the disproportionation of tracer uranium^{V}, neptunium^{V}, plutonium^{IV}, and the corresponding reproportionation reactions. In the absence of surface catalysis, such reactions will be exceedingly slow. The second is concerned with the solubility and carrying of neptunium^{V}. According to Katz and Seaborg[3] macroscopic neptunium^{V} fluoride is soluble, but according to Hyde[4] the tracer is carried on lanthanum fluoride precipitates. As a result of situations like these the investigator must be continually on guard against begging the question.

The recognised oxidation states of uranium, neptunium and plutonium in aqueous solution are summarised in Table I.

TABLE I.—OXIDATION STATES OF URANIUM, NEPTUNIUM, PLUTONIUM IN AQUEOUS SOLUTION

Oxidation state	Uranium	Neptunium	Plutonium
III	Oxidised by water to uranium^{IV}	Rapidly oxidised by dissolved oxygen	Stable
IV	Stable	Stable	Stable
V	Disproportionates to uranium^{IV} and uranium^{VI}	Stable	Thermodynamically unstable
VI	Stable	Stable	Stable

It is well known that 2-thenoyltrifluoracetone (TTA) in benzene is a good extracting agent for actinide elements in the +4 oxidation state at low pH values[3,5] and that lanthanum fluoride carries all oxidation states of the actinides except the +6 state.[4] It was therefore decided to use a combination of these methods as the basis for a determination scheme. Although at low concentrations plutonium^{V} is fairly stable in the pH range 2 to 7,[6] its behaviour during extraction has not been previously determined. Marklen and McKay[7] have assumed that it is not extracted by TTA and Connick[8] has concluded that it is carried on a lanthanum fluoride precipitate.

EXPERIMENTAL

Tracers

Uranium-237 was produced by irradiating enriched uranium-236 oxide with thermal neutrons in the MTR at Arco, Idaho.

Neptunium-239 was produced by irradiating depleted uranium-238 metal with thermal neutrons.

Plutonium-237 was produced by bombarding enriched uranium-235 with 30 MeV alpha particles in the University of California 60-inch cyclotron.

In each case the target material was dissolved in hydrochloric acid and purified by ion exchange.[9,10] The radiochemical purity was established by gamma-ray spectrometry and by decay measurements during the course of experimental work.

Reagents

2-*Thenoyltrifluoracetone*, obtained from the Peninsular Chemical Research, Inc., Gainesville, Florida was used without further purification. Otherwise, natural sea water and reagent-grade chemicals were used throughout.

Preparation of stock solutions

Uranium^{IV} was prepared by passing uranium-237 tracer solution containing 2 mg of normal uranium in $4M$ hydrochloric acid through a 0·4-cm × 10-cm lead reductor column.[11]

Uranium^{VI}, *neptunium*^{VI} and *plutonium*^{VI} were all prepared by evaporating the tracer to dryness with nitric acid and taking up the residue with $0{\cdot}05M$ perchloric acid and $0{\cdot}005N$ potassium dichromate.

Neptunium^{IV} tracer was prepared by evaporating the neptunium tracer solution to dryness and dissolving with a warm solution of $0{\cdot}5M$ hydrochloric acid, $0{\cdot}1M$ potassium iodide and $0{\cdot}1M$ hydrazine hydrochloride. Attempts to prepare neptunium^{IV} quantitatively with potassium iodide or hydroxylamine or both, and by back-extraction from 2-thenoyltrifluoroacetone with $8M$ hydrochloric acid did not produce solutions with the expected properties.

Plutonium^{III} was prepared by evaporating the tracer to dryness and dissolving the residue in $0{\cdot}6M$ hydrochloric acid and hydroxylamine solution.

Plutonium^{IV} tracer was prepared by evaporating the solution to dryness with hydroxylamine and dissolving the residue in a dilute nitric acid and sodium nitrite solution.

Extraction procedure

A 10-ml portion of the aqueous solution was adjusted to the appropriate pH with hydrochloric acid or ammonium acetate and "spiked" with a μlitre portion of tracer solution in a given oxidation state. An equal volume of $0{\cdot}4M$ 2-thenoyltrifluoroacetone in benzene was added and the total solution was shaken for approximately 10 min. The phases were separated and a 4-ml aliquot of each phase was pipetted into a glass tube and counted in a well crystal scintillation counter.

Precipitation procedure

A 25-ml portion of solution was "spiked" with a μlitre portion of tracer solution in a given oxidation state, followed by the addition of 2·5 mg of lanthanum carrier and 1 ml of hydrofluoric acid. The solution was stirred for 2 min and centrifuged. The supernatant solution was decanted and the precipitate dissolved, without washing, in a mixture of 1 ml of saturated boric and 1 ml of concentrated hydrochloric acid. The volume was adjusted to equal that of the supernatant solution and gamma-ray assay was performed on both portions.

RESULTS

The results in Table II show that the extraction of uranium^{VI} increases with an increase in the pH from 0·4 to 4·2. Uranium^{IV} is extracted. The extraction of the hexavalent form could be the result of the increase in the effective ligand concentration with the increase in pH on the addition of dilute aqueous ammonia

TABLE II.—PER CENT EXTRACTION OF U^{IV} AND U^{VI} BY $0{\cdot}4M$ TTA *vs.* pH IN THE ABSENCE OF ACETATE IONS

pH	U^{IV}	U^{VI}
0·4	94·5	1·1
1·7	—	73·6
2·3	—	96·9
3·1	—	99·3
4·2	98·5	99·5

Table III shows the effect of acetate concentration upon the extraction of uranium^{IV} and uranium^{VI} at pH 4·2. The extraction of uranium^{VI} decreases with an increase in the molarity of the ammonium acetate whereas uranium^{IV} is extracted at all molarities. It would take approximately $11M$ ammonium acetate to complex almost all of the hexavalent state in order to prevent its extraction by TTA.

The per cent extraction of the oxidation states of uranium, neptunium and plutonium from distilled water and sea water at various values of pH are given in Table IV. The results are averages of at least duplicate determinations. It is seen that pH 0·3–0·4 is favourable for separating the 4-oxidation states from the remaining oxidation states by the extraction procedure.

TABLE III.—PER CENT EXTRACTION OF U^{IV} AND U^{VI} BY 0·4*M* TTA *vs.* ACETATE CONCENTRATIONS AT pH 4·2

Ammonium acetate, *M*	U^{IV}	U^{VI}
0·55	96·5	96·4
2·20	95·6	35·9
4·40	97·3	22·5
8·80	96·8	9·7
11·00	97·8	4·4

In the case of uranium^{IV}, repeated separations performed 2 hr apart on different aliquots showed increasing activity in the raffinate from the extraction and in the supernatant solution from the precipitation. Because this indicates gradual atmospheric oxidation of uranium^{IV}, the earliest recorded results have been taken as the most indicative of uranium^{IV} behaviour.

At pH 4·2 plutonium^{III}, plutonium^{IV}, uranium^{IV} and neptunium^{IV} are extracted.

TABLE IV.—PER CENT EXTRACTION OF URANIUM, NEPTUNIUM AND PLUTONIUM OXIDATION STATES BY 0·4*M* TTA FROM DISTILLED WATER AND SEA WATER AT VARIOUS VALUES OF pH

State	pH	Distilled water	Sea water
U^{IV}	0·3	93·3	94·3
	1·5	97·5	98·4
	4·3*	98·8	98·7
U^{VI}	0·4	3·4	1·7
	4·3*	4·4	3·6
Np^{IV}	−0·3	87·7	80·1
	0·3	98·7	98·8
	4·3*	100·0	92·0
Np^{VI}	0·3	0·1	0·1
	4·1	0·2	5·0
Pu^{III}	0·0	3·5	1·2
	0·3	4·6	2·8
	1·1	10·5	7·5
	2·0	—	79·4
	4·3*	99·0	100·0
Pu^{IV}	0·3	95·1	96·5
	4·2*	98·2	99·5
Pu^{VI}	0·0	0·1	5·2
	0·3	0·5	9·2
	4·2*	2·9	3·5

* Ammonium acetate is >10*M*.

The per cent of each oxidation state carried by lanthanum fluoride precipitation in the presence and absence of uranyl ion holdback or hydrochloric acid is given in Table V.

TABLE V.—PER CENT CARRYING OF URANIUM, NEPTUNIUM AND PLUTONIUM OXIDATION STATES ON LANTHANUM FLUORIDE FROM DISTILLED WATER AND SEA WATER UNDER VARIOUS CONDITIONS

State	Without UO_2^{2+} carrier		With UO_2^{2+} carrier	
	No HCl	1 ml of HCl	No HCl	1 ml of HCl
	Distilled water			
U^{IV}	—	—	97·3	98·2
U^{VI}	—	20·0	—	3·8
Np^{IV}	95·9	96·2	96·2	97·4
Np^{VI}	18·2	13·4	4·6	3·8
Pu^{III}	94·5	93·5	94·4	95·6
Pu^{IV}	—	—	—	99·0
Pu^{VI}	18·0	10·2	3·0	3·8
	Sea water			
U^{IV}	—	91·5	98·9	96·9
U^{VI}	40·1	3·4	34·6	2·6
Np^{IV}	94·6	97·6	96·2	99·1
Np^{VI}	39·7	1·6	27·9	1·3
Pu^{III}	96·4	97·8	97·4	97·5
Pu^{IV}	99·0	—	99·0	98·0
Pu^{VI}	14·0	3·6	12·5	5·0

Here again, the uranium results, as well as those for neptunium and plutonium, are averages of at least duplicate determinations. No design experiments were run to determine the optimum amounts of uranium and lanthanum carriers. It was noted, however, that less than 2·5 mg of lanthanum carrier was insufficient to carry all of the uranium^{IV}. With the exception that hydrofluoric acid was the last reagent added, no preferred order of reagent addition was noted. Without uranyl ion holdback carrier, as is seen in Table V, uranium^{VI} tends to coprecipitate with lanthanum fluoride from distilled water. The best results were achieved using both 2 mg of uranyl ion and 1 ml of hydrochloric acid.

The results for neptunium and plutonium in Table IV are in general agreement with those of Lai, *et al.*[12] which are presented in Table VI.

We did not obtain any results for neptunium^{V} in distilled water or sea water. Because little difference in the behaviour of the other actinide oxidation states between distilled water, salt water and sea water has been noted, and because the +5-state should be least affected by complex ion formation, the results with sodium chloride solutions have been taken as being applicable to the other two media.

It is seen from Tables IV and V that near-optimum conditions for neptunium oxidation state separation correspond closely to those used for uranium, namely, a pH of 0·4 for extraction and the use of uranyl ion holdback carrier and hydrochloric acid for precipitation. In the case of uranium, either the extraction at low pH or the precipitation method could be used to distinguish between uranium^{IV} and uranium^{VI}.

Table VI.—Per cent extraction and carrying of neptunium and plutonium oxidation states from sodium chloride solution

State	TTA Extraction, pH 0·4	TTA Extraction, pH 4·2	LaF_3 precipitation, 2 mg of UO_2^{2+}
Np^{IV}	—	97–100	96
Np^{V}	—	0–5	95–100
Np^{VI}	—	2[b]	2
Pu^{III}	4	98–100	96
Pu^{IV}	97–100	97–100	96
Pu^{V}[b]	not extracted	not extracted	carried
Pu^{VI}	4	5–12[a]	4

[a] See section on Results.

[b] Predicted behaviour.

Lai prepared neptunium^{V} by fusing the tracer in sodium chloride for 1 hr at 850°–875°, cooling and dissolving the residue in dilute hydrochloric acid.

In the case of neptunium, because of the additional oxidation state, both methods must be used. The results are then interpreted as

$$Np(TTA) = Np^{IV}$$
$$Np(Raf.) = Np^{V} + Np^{VI}$$
$$Np(LaF_3) = Np^{IV} + Np^{V}$$
$$Np(Sup.) = Np^{VI}$$
$$Np(Total) = Np^{IV} + Np^{V} + Np^{VI}$$

where, for simplicity, separations are written as being quantitative. This over-determined system of five equations in three unknowns can then be solved by the method reported by Wilson[13] in order to obtain the most consistent distribution.

It is seen that near optimum conditions for extracting plutonium^{IV} or holding plutonium^{VI} in solution during lanthanum fluoride precipitation correspond closely to those found for uranium. In the case of plutonium, because of its additional oxidation state, two extractions and a lanthanum fluoride precipitation must be carried out. The first extraction is done from pH 0·4 solution. The aqueous phase may then be adjusted to 4·2.

The behaviour of plutonium^{VI} towards extraction did not agree with that expected from the results of Heisig and Hicks[14] because of the acetate concentration. It appears that the plutonium^{VI} is complexed during the extraction.

As in the case of neptunium, the lanthanum fluoride precipitation should then be carried out on a separate aliquot. The results are then interpreted as

$$Pu(TTA, pH\ 0{\cdot}4) = Pu^{IV}$$
$$Pu(TTA, pH\ 4{\cdot}2) = Pu^{III}$$
$$Pu(Raf., pH\ 4{\cdot}2) = Pu^{V} + Pu^{VI}$$
$$Pu(LaF_3) = Pu^{III} + Pu^{IV} + Pu^{V}$$
$$Pu(Sup.) = Pu^{VI}$$
$$Pu(Total) = Pu^{III} + Pu^{IV} + Pu^{V} + Pu^{VI}.$$

Here again, separations have been written as being quantitative, and again, the unknowns are overdetermined.

DISCUSSION

Ideally, in order to demonstrate that two oxidation states of the same tracer element can be separated from each other by a given procedure, is should be shown that:

(1) tracer solutions have been prepared for each state, and that in each solution the given state is quantitatively maintained;

(2) the states are not altered by the separation process, and the results of the separation process are not affected by the substances introduced with the tracer (*e.g.*, oxidising or reducing agents);

(3) the separation is quantitative.

In practice, the second requirement may be modified with regard to oxidation state perturbation. Provided that sequential separation procedures are not utilised, it is only necessary that the final states be separable, and that the separated quantities correspond to the original distribution. For example, consider the LaF_3 method in separating the two oxidation states neptunium^{IV} and neptunium^{VI}. The neptunium^{VI} remains in the supernate and the neptunium^{IV} is coprecipitated. Now, if the procedure changes the oxidation state of neptunium^{IV} to neptunium^{V}, and neptunium^{V} coprecipitates when present, no error is incurred by overlooking the change, provided the supernate is not subjected to any further separations. The investigator must consider each case on individual merit and decide whether likely redox effects are or are not going to lead to bias in his results.

The above ideal has been approached in varying degrees by the methods described. What has been achieved is a self-consistent interpretation of a series of preparation and separation procedures, which is also consistent with published procedures for, and properties of, the various oxidation states, the procedures being "nearly quantitative." This interpretation is summarised in Table VII.

TABLE VII.—SUMMARY OF OXIDATION STATE BEHAVIOUR OF URANIUM, NEPTUNIUM AND PLUTONIUM AT TRACER CONCENTRATIONS

Precipitation by LaF_3		Extraction by TTA	
		pH 0·4	pH 4·3
M^{3+}	Carried	Not extracted	Extracted
M^{4+}	Carried	Extracted	Extracted
MO_2^{+}	Carried	Not extracted	Not extracted
MO_2^{2+}	Not carried	Not extracted	Extracted, unless complexed

Without further information, it is uncertain whether lack of quantitativeness in the separations results from the behaviour of the oxidation state, the presence of small fractions of other oxidation states in the stock solutions, or partial changes of oxidation state by the procedure. In some instances, this could be determined by re-extraction or reprecipitation. If the same distribution ratio were obtained for successive performances of the same separation, it could then be argued that the species was originally present in pure form. The use of inert carriers in the extraction procedures might serve to sharpen separations and should also be tried.

In practice[15] for a solution containing all three elements, the following separation scheme is adhered to. First a 25-ml portion of the solution is made 0·5*M* with respect to hydrochloric acid and the uranium^{IV}, neptunium^{IV} and plutonium^{IV} are extracted with an equal volume of 0·4*M* 2-thenoyltrifluoracetone for 10–15 min. The pH of the raffinate is then raised to 4·3 with 11*M* ammonium acetate, and plutonium^{III} is extracted with a second portion of 2-thenoyltrifluoracetone. The lanthanum fluoride carrying step is then performed on a separate 25-ml portion of the solution being analysed. In rapid succession, 2 mg of natural uranium holdback carrier, 2·5 mg of lanthanum carrier, 1 ml of hydrochloric acid and 1 ml of hydrofluoric acid are added. Uranium^{VI}, neptunium^{VI} and plutonium^{VI} remain in the supernatant solution. Radiochemical analysis of each fraction is then carried out using Wish's method.[10] The results may then be interpreted using the equations described above, or more general equations may be used to incorporate the distribution ratios present.

Acknowledgement—This work was partially supported by the U.S. Atomic Energy Commission's Division of Research.

Zusammenfassung—Der vorliegende Bericht beschreibt die Entwicklung, Erprobung und Anwendung chemischer Methoden zur Ermittelung der Verteilung von Uran, Neptunium und Plutonium in ihren verschiedenen Wertigkeitsstufen in wässrigem Medium und bei Anwesenheit in Tracermengen. Die erzielten Trennungen sind in der Grössenordnung von 95%. Die mitgeteilten Daten zeigen die perzentuelle Extraktion der drei Metalle in ihren verschiedenen Oxydationsstufen durch 0,4 m 2 Thenoyltrifluoroazeton bei verschiedenen pH-Werten. Radiochemische Analyse wurde auf die Bestimmungen in den Fraktionen angewandt.

Résumé—Ce rapport décrit le développement, l'essai et l'application d'un procèdé chimique pour déterminer les répartitions des différents degrès d'oxydation de l'uranium, du neptunium et du plutonium dans divers milieux aqueux à l'état de traces. Les séparations effectuées donnent une pureté de l'ordre de 95%. Les résultats indiquent le pourcentage d'extraction par la 2 thénoyltrifluoracétone 0,4 M des degrès d'oxydation de l'uranium, du neptunium et du plutonium à différentes valeurs de pH et le pourcentage donné par le fluorure de lanthane à partir de l'eau distillée et de l'eau de mer dans diverses conditions. L'analyse radiochimique des parties fractionnées peut alors être utilisée pour déterminer les séparations demandées des degrès d'oxydation.

REFERENCES

[1] N. E. Ballou, *Calculated Activity Contributions of Nuclear Weapon Produced Neutron Induced Radionuclides*, USNRDL-TR in preparation.

[2] E. C. Freiling and N. E. Ballou, *Nature*, 1962, **195,** 1283.

[3] J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements.* John Wiley and Sons, Inc., N.Y., 1957.

[4] E. K. Hyde, *Radiochemical Separations of the Actinide Elements.* Chapter 15 of *The Actinide Elements*, NNES IV-14A. McGraw-Hill Book Co., N.Y., 1954.

[5] A. M. Poskanzer and B. M. Foreman, Jr., *J. Inorg. Nuclear Chem.*, 1961, **16,** 323.

[6] L. H. Gevantman and K. A. Kraus, *Chemistry of Plutonium (V). Stability and Spectrophotometry.* Paper 4.16 of *The Transuranium Elements*, NNES IV-14B. McGraw-Hill Book Co., N.Y. 1949, p. 500.

[7] T. L. Marklen and H. McKay, *J. Inorg. Nuclear Chem.*, 1958, **7,** 298.

[8] R. E. Connick, *Oxidation States, Potentials, Equilibria and Oxidation Reduction Reactions o Plutonium.* Chapter 8 of *The Actinide Elements*, NNES IV-14A. McGraw-Hill Book Co., N.Y. 1954, p. 251.

[9] L. Wish and M. Rowell, *Sequential Analysis of Tracer Amounts of Np, U, and Pu in Fission-Product Mixtures by Anion Exchange*, USNRDL-TR-117, 11 Oct. 1956.

[10] L. Wish, *Analyt. Chem.*, 1959, **31,** 326.

[11] W. O. Cook, F. Hazel and W. M. McNabb, *ibid.*, 1950, **22,** 654.

[12] J. R. Lai, S. C. Foti, C. M. Callahan and E. C. Freiling, unpublished work.

[13] D. I. Wilson, *Analyt. Chem.*, 1958, **30,** 1578.

[14] D. L. Heisig and T. E. Hicks, *The Distribution of* Pu(VI) *and* Pu(III) *in Theonyltrifluoroacetone-Benzene-Nitric Acid Mixtures*, UCRL-1664, 2 February 1952.

[15] S. C. Foti and E. C. Freiling, *Oxidation States of* U^{237} *and* Np^{239} *in Underwater Burst Debris*, USNRDL-TR-370, 24 Sept.. 1959.

Talanta, 1964, Vol. 11, pp. 393 to 403. Pergamon Press Ltd. Printed in Northern Ireland

SOME OBSERVATIONS ON THE ZERO-CURRENT BEHAVIOUR OF ANTIMONY INDICATOR ELECTRODES

E. BISHOP and G. D. SHORT*
Washington Singer Laboratories, The University, Exeter, Devon, England

(*Received* 21 *June* 1963. *Accepted* 14 *August* 1963)

Summary—Methods are described for the preparation and handling of antimony electrodes of precise area and good reproducibility, and for the determination of potential-pH and potential-log P_{O_2} relationships under controlled conditions. Conditions affecting the response characteristics are defined and critically examined: they include the purity of the antimony, the history of the electrode, the temperature, agitation, poising, ionic strength and composition of the solution, the working pH range, the condition of the electrode surface and the oxygen content of the solution. The marked influence of the presence of buffering materials, of the condition of the electrode surface and of the oxygen content of the solution are emphasised. Phosphates cause changes of the electrode surface. The current situation is reviewed in the context of the present work, and electrode mechanisms are discussed.

DURING the course of fundamental investigations of the differential electrolytic potentiometry of acid-base reactions[1] and of the polarisation of antimony electrodes,[2] the necessity arose for a close enquiry into the zero-current behaviour of antimony electrodes.[3] Despite the general superiority of the glass electrode, antimony, the best of the metal-metal oxide electrodes, has advantages of cheapness, simplicity, robustness, ease of fabrication, cleaning and activation, comparative insensitivity to poisoning, low impedance, a reasonable exchange current and fast response speed, and claims continuing interest in many situations, such as in non-aqueous titrimetry,[4] and in polarisation methods.[1] The literature, however, contains much confusion and contradiction, and not until comparatively recently has this been recognised[5,6] as probably arising from a lack of standardisation of conditions of preparation, handling and use of the electrodes, in turn the result of a lack of appreciation of influential factors. This derogates much of the virtue of earlier work on the subject. The present investigation was undertaken in the hope of resolving some of the points of contention, and it has been thought worth offering a summary of the current situation. To avoid repetition, the present work is intermingled as comment with the review.

EXPERIMENTAL

Preparation of electrodes

Spectrographically pure antimony (Johnson Matthey Ltd.) is melted in a quartz crucible in air. A short length (the bottom) of Pyrex tubing of appropriate diameter sealed to a 5-inch length (the top)

---

* Present address: Chemistry Department, Massachusetts Institute of Technology, Cambridge 39, Mass., U.S.A.

of 10-11-mm tubing is clamped vertically with the lower end just above the molten antimony. The tube is preheated by flaming and lowered to dip into the molten antimony, and the liquid metal is drawn into the tube to about 1 cm above the seal by suction applied from a rubber bulb attached to the top. A tight metal-glass junction results on cooling, and electrical contact is effected by pouring molten solder into the upper tube and sealing into this a length of tinned copper wire. The connecting lead is fixed at the top with wax, and a fresh surface of antimony is exposed at the bottom by cutting off a slice of the assembly at 90° to the tube axis with a diamond wheel. A plane surface of area equal to the internal cross-section of the tube is obtained. Many sets of electrodes were made of areas ranging from 0·126 cm^2 to 0·00102 cm^2, mean diameters being determined by a vernier microscope. Matched pairs of micro electrodes are made by drawing out a thick-walled capillary, cutting in the middle and sucking antimony into the two sections. Larger, cylindrical electrodes are made by cutting back the glass sheath to expose a rod of metal.

Electrodes are usable immediately after sawing, or may be aged (oxidised) by storage in water. No pre-treatment other than wiping with tissue before use has been found necessary—a process now meeting with general acceptance.[7] Electrodes are never allowed to dry out.

Reagents

Water, of chloride, nitrogen and silica content less than $10^{-11}M$, prepared in a quartz still,[8] is boiled out in borosilicate glass, handled under nitrogen in polythene, and protected from carbon dioxide as previously described.[1] This water, never stored for more than 36 hr, is used throughout the experimental work and for the preparation of all solutions.

Carbon dioxide-free perchloric acid solutions are prepared as required by dilution of standardised 0·1*M* solutions prepared from the 72% AnalaR acid.

Barium hydroxide solutions are prepared as before.[1]

The background electrolytes, usually potassium chloride, occasionally sodium sulphate, of AnalaR grade, are selected for neutral reaction. Buffer and other materials are of AnalaR grade. Calibrated glassware is used throughout.

Procedure

(*a*) *Potential-pH measurements:* A 400-ml beaker is charged with 200 ml of water and 0·5 g of potassium chloride ($\doteq$0·03*M*) and fitted with a cover carrying a mounted set of three (or more) antimony electrodes, a calibrated E.I.L. GHS23 lithium-barium glass electrode, the salt bridge, terminated with a low leakage rate ceramic plug, a high-capacity saturated calomel cell of area 30 cm^2, a burette and a gas inlet which so dips into the solution that gas bubbles do not break on the electrode surfaces. Coating the beaker with hard paraffin wax to obviate attack of the glass and dissolution of alkali was found to make no difference to the results. The solution is magnetically stirred just at cavitation speed with a PTFE-coated paddle of a length just less than the diameter of the beaker. The potentials of the electrodes with respect to the reference electrode are read on an E.I.L. model 23A pH meter, from which a Cambridge DE 2-sec recorder is driven. By means of helipots, the recorder scale can be expanded and backed off to provide more sensitive discrimination and to observe potential drift. Scale expansion to incipient noise level can also be used to overcome recorder dead space in establishing the attainment of equilibrium and in examining low drift rates. Electrode circuits are selected by a Doran high impedance switching unit. An interval of at least 30 min is allowed for potential equilibration at each pH value, and the pH is changed by addition of increments of 0·001*M* perchloric acid or 0·0005*M* barium hydroxide from the burette. More concentrated solutions are used outside the pH range 4–10. Supplementary results are provided from numerous perchloric acid—barium hydroxide titrations.[1] A vigorous stream through the solution of the appropriate gas at constant pressure is maintained throughout.

(*b*) *Variation of partial pressure of oxygen:* As in (*a*), with the addition that pure oxygen and "oxygen-free" (white spot) nitrogen are passed through separate banks of calibrated rotameters of sizes such that a nominal variation from 0·1% to 100% of oxygen in the gas stream bubbling through the solution can be effected. The gas flow from the cylinder reducing valves is further regulated by calibrated needle valves. The attainment of potential equilibrium is observed on the recorder trace, and a series of measurements is started with the lowest required oxygen partial pressure because equilibration is much more rapid in the direction of increasing oxygen concentration.

Each series of experiments was replicated many times, both with the same and with fresh electrodes and/or solutions, and each run was carried out with at least three electrodes. Replicability is discussed below. Sets of results are illustrated graphically in Figs. 1 and 2. The laboratory was thermostatted at 20°. The pH values indicated by the glass electrode agreed with those calculated from solution composition.

REVIEW, RESULTS AND DISCUSSION

Factors recognised[9] as affecting the performance of antimony electrodes in aqueous media are:

(*a*) the purity of the antimony and the history of the electrode;
(*b*) temperature and agitation of the solution;
(*c*) the poising, ionic strength and composition of the solution;
(*d*) the working pH range;
and (*e*) the oxygen content of the solution or partial pressure of oxygen in the atmosphere in contact with the solution.

It is therefore necessary to describe meticulously the preparation, handling and conditions of use of the electrodes if the results are to be of significance and their validity is to be appraised. The factors will be discussed as grouped above.

Potential-governing equilibria of metal–metal oxide electrodes

Imprimis, as a metal–metal oxide electrode, it is tacitly assumed that the following equilibria are applicable:

$$Sb_2O_3 + 3H_2O \rightleftharpoons 2Sb(OH)_3 \qquad (1)$$

$$Sb(OH)_3 \rightleftharpoons Sb^{3+} + 3OH^- \qquad (2)$$

whence the solubility product $S_{Sb_2O_3}$ is

$$S_{Sb_2O_3} = [Sb^{3+}][OH^-]^3 = [Sb^{3+}]\frac{K_w{}^3}{[H^+]^3} \qquad (3)$$

and that the electrode responds to antimony^{III} ions by the Nernst relationship

$$E = E_{0_{Sb/Sb^{3+}}} + \frac{RT}{3F}\log_e [Sb^{3+}] \qquad (4)$$

From (3) and (4)

$$E = E_{0_{Sb/Sb^{3+}}} + \frac{RT}{3F}\log_e S_{Sb_2O_3}\frac{[H^+]^3}{K_w{}^3} \qquad (5)$$

$$= E_{0_{Sb/Sb^{3+}}} + \frac{RT}{3F}\log_e \frac{S_{Sb_2O_3}}{K_w{}^3} + \frac{RT}{3F}\log_e [H^+]^3 \qquad (6)$$

The first two terms on the right hand side of (6) are assumed to be constant, and may be combined as the single term E_0', so that

$$E = E_0' + \frac{RT}{F}\log_e [H^+] = E_0' - \frac{2{\cdot}303RT}{F}\,pH \qquad (7)$$

DISCUSSION

Equilibria (1) and (2) can be strongly challenged. The hydration process is undoubtedly complex, and strongly dependent on conditions; it may be represented by

$$aSb_2O_3 + (3a - 2b)H_2O \rightleftharpoons 2Sb_aO_b(OH)_{(3a-2b)} \qquad (8)$$

and it is unlikely that Sb^{3+} ions will be formed, of a concentration adequate to control electrode potentials, the over-all ionisation being either

$$Sb_aO_b(OH)_{(3a-2b)} \rightleftharpoons Sb_aO_b{}^{(3a-2b)+} + (3a - 2b)OH^- \qquad (9)$$

or

$$Sb_aO_b(OH)_{(3a-2b)} \rightleftharpoons Sb_aO_{(3a-2b)}{}^{(3a-2b)-} + (3a - 2b)H^+ \qquad (10)$$

with an isoelectric region of overlap of the two modes of ionisation, which are themselves complex equilibria. This does not affect the pH dependence, because the relevant term in either case resolves to

$$\frac{RT}{(3a - 2b)F} \log_e [H^+]^{(3a-2b)} = \frac{RT}{F} \log_e [H^+] \qquad (11)$$

but the constancy of the term E_0' is no longer assured, and the second term in (6) may well vary with conditions. This possibility has not received sufficient attention in the past, but suspicion has recently been turned upon the constancy of normal electrode potentials.[7]

(*a*) *Purity and history of the electrode*

After early confusion, Perley's careful work established the detrimental effects of traces of copper, which are now confirmed; but otherwise antimony is comparatively insensitive to impurity,[6] notably to arsenic and sulphur.[10] Many methods of preparation have been examined.[6,11] Electrodeposition gives variable quality[6] because of deficiency of oxygen in the metal lattice, inclusion of electrolyte (*cf.* "explosive" antimony[12]) and variable surface activity. Casting in air is found to give the most satisfactory electrodes. Compression of mixtures of powdered metal and oxide[11] has been advocated for ensuring uniform distribution of oxide.

Pretreatment to secure a clean reproducible surface by electrolysis,[13] chemical activation,[13] abrasion[14] and scraping[15] has been advocated; simple wiping with tissue has been found perfectly satisfactory. Electrodes after drying out, or prolonged storage in aerated water, behave erratically when returned to use because of too thick an oxide film on the surface. Activity is quickly restored by the differentiating current in DEP,[1] so that cathodic polarisation at $\sim 10\ \mu A\ cm^{-2}$ is effective; but normal practice is to saw a thin slice off the end of the electrode to expose a fresh surface. The electrode is then used immediately, or after ageing for 24–48 hr in aerated water. Electrodes are not exposed to solutions outside the pH range 2–10, otherwise marked hysteresis occurs. Electrodes prepared and handled as described show good reproducibility (± 5 mv). No specific area effects[16] have been observed.

(*b*) *Temperature and agitation of the solution*

The scant work on temperature effects[17] indicates far from theoretical behaviour at temperatures above 30°, and no consistent theory has been advanced to account for the deviations. The present work has been confined to a temperature of 20°, but polarisation measurements up to 50° have been analysed.[2a]

Stirring affects the electrode potentials.[9,14,18] The effect has been reviewed,[6] and Gatty and Spooner have plausibly applied the local action theory of corrosion.[9] The electrode surface consists of anodic (bare metal) and cathodic (oxide layer) sites, and the advent of dissolved oxygen increases the proportion of cathodic sites, causing a positive potential drift. Stirring either increases the rate of diffusion of oxygen to the bare metal, to increase the proportion of cathodic sites causing a positive deviation, or enhances anodic dissolution to expose more bare metal, causing a negative drift; both effects have been observed under appropriate conditions.[9] The versatility of the theory makes it difficult to prove or disprove the interpretation of a given observation.

(*c*) *Poising, ionic strength and composition of the solution*

Poising: Perley[14] alone appears to have observed that the potential at a fixed pH differs in the presence or absence of buffering substances. That good linear plots of near theoretical slope result from calibration of the electrode in a series of buffer solutions is no guarantee that the behaviour will be similar in unpoised solutions, or in solutions of low buffer concentration or low ionic strength. For example, at pH 7 and 20° in a pure oxygen atmosphere, the antimony electrode potential with respect to the SCE was -320 mv in unpoised solution. Addition of ammonium acetate (pH 6·98) lowered the potential to -356 mv. In ordinary nitrogen ($\sim$1 % oxygen) these potentials became -405 ± 5 and -411 ± 2 mv, respectively. Change of atmosphere may cause a change in electrode reaction,[9,20] or removal of oxygen overvoltage;[20] but the negative shift on addition of buffer is unlikely to be caused by reduction of the solubility of oxygen on the addition of electrolyte[6] because the high supporting electrolyte concentration ensures that the ionic strength is hardly altered. The concentration of ammonium acetate is not critical; variation from 0·005M to 0·03M made no significant difference to the potentials.

Ionic strength: Effects claimed to result from changes in ionic strength[14,21,22] can more probably be ascribed to adventitious addition of impurities with the electrolytes, to change in hydrogen ion activity, or to change in oxygen solubility,[6] or, at low ionic strengths, to activation overpotential.

Composition of solution: Oxidising, reducing or complexing (particularly oxygen-ligand) substances will naturally affect the potential of the antimony electrode by upsetting the equilibria on which it depends. For example, buffers containing tartrate or citrate must be avoided.[23] Silver[24] and copper ions, and, presumably, other metal ions, such as mercury, displaceable by antimony, produce abnormal potentials. The effect of phosphate ion is discussed below.

(*d*) *Working pH range. Potential-pH relationships and* E_0' *values*

Linearity, slope and range of response: The reasonably linear pH response has repeatedly been affirmed, but it is generally recognised that the useful range is limited to pH 1–12, and that excursions to these limits give rise to hysteresis, so that the electrode functions best in the range pH 3 to 10. Most results refer to calibration in aerated buffer solutions. Perley, however, has shown[14] that different slopes for the emf-pH plot result, depending on whether the solution pH is greater or less than 8: a break occurs in the region around neutrality. Others have noted this phenomenon.[15] The emf-pH plots of Fig. 1 show that for unbuffered, oxygenated solutions, the antimony electrode yields a line of slope 58 mv/pH unit over the range pH 3–6 in agreement with Perley's results; but the plot becomes non-linear at higher pH values,[25] and shows a flat portion over the range pH 6·5–7·5, somewhat resembling that observed by Kolthoff and Hartong.[15] Under ordinary ($\sim$1 % of oxygen) nitrogen, the slope in the region pH 8–11 is 52 mv/pH unit, again in agreement with Perley's results. The effect of oxygen is greatest in unpoised neutral or weakly alkaline media, and addition of buffer causes an immediate negative shift of potential towards the value in nitrogen. The change in slope could well indicate a change in active ion from hydrogen to hydroxyl, *i.e.*, a change in electrode order, as happens with silver-halide systems,[16] or of electrode reaction [*cf.* refs. (9) and (10)].

Formal potential, E_0': Assuming that equation (7) is valid, extrapolation of the emf-pH plot should give values for E_0', but in practice the extrapolation extends over 2–8 orders of concentration, casting doubt on its reliability. Moreover, slopes vary between 50 and 60 mv/pH unit; potentials at a given pH value may vary by 100 mv according to the conditions of measurement; and temperature coefficients are uncertain. The diversity of reported E_0' values[6] is not surprising, and any attempt to draw conclusions from such evaluations must be approached with caution. Pourbaix *et al.*[26] give the theoretical value of E_0' on the hydrogen scale as 0·167 v: most quoted values are about 0·1 v higher.[6] Values from Fig. 1 are 0·274 v in a pure oxygen atmosphere, and 0·245 v in ordinary nitrogen. Mehta and Jatkar,[27] surveying a large number of reported values, discern a tendency towards the formation of two distinct groups, one around 0·275 v, the other around 0·25 v. It is tempting to ascribe the higher value to determinations in aerated or oxygenated solutions, and the lower to de-aerated solutions; but the correlation is vitiated by certain exceptions and by lack of definition of experimental conditions.

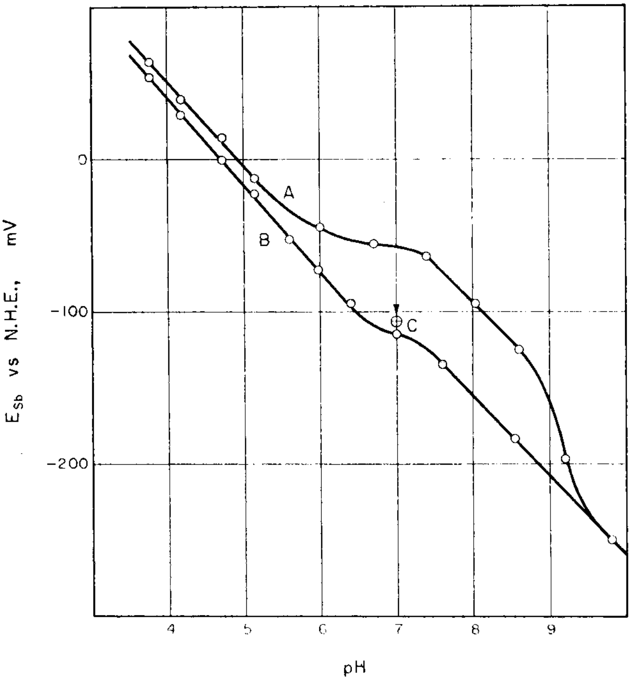


FIG. 1.—Emf—pH relationships of antimony electrodes.
Curve A: In an atmosphere of pure oxygen. Point C illustrates the effect of the addition of a buffering material to the solution.
Curve B: In an atmosphere of nitrogen containing a trace (about 1%) of oxygen. Potentials have been converted to the hydrogen scale using the value 0·245 v for the SCE.

Under customary conditions, the electrode does not accord with the simple concept (7), but does approach theoretical behaviour under strictly anaerobic conditions[17,28] for which E_0' values of 0·16 v have been reported, and deoxygenation shifts the potentials towards the theoretical values. The electrode reaction must therefore be complex rather than simple, *e.g.*, (8), and may be a mixed process. For instance,

$$2Sb + 3H_2O \rightleftharpoons Sb_2O_3 + 6H^+ + 6\varepsilon \tag{12}$$

gives a potential linearly dependent on pH, and an E_0' value of 0·16 v, while

$$O_2 + 4H^+ + 4\varepsilon \rightleftharpoons 2H_2O \tag{13}$$

gives the same pH dependence and an E_0 value of 1·23 v, but the potential is also dependent on log P_{O_2}. At a constant partial pressure of oxygen, the electrode should show a linear pH response, with an E_0 between 0·16 and 1·23 v, depending on the partial pressure of oxygen and the state of the electrode surface. Several theories attempt a more detailed mechanistic explanation,[9,20] probably the most successful being the local action theory of corrosion; but none has yet been completely vindicated. Clearly, however, the buffering and oxygen content of the solution are intimately involved in the response of the electrode, and the E_0' value is a function of conditions of use.

(*e*) *Oxygen response of antimony electrodes*

Most reports refer to aerated solutions, one or two to pure oxygen or pure nitrogen atmospheres. Tourky and Moussa[20] examined the response in carefully de-aerated solutions of electrodes prepared in an atmosphere of hydrogen, and found a step-like emf-pH plot with alternating high and low slopes showing five breaks which they attempted to interpret in terms of neutralisation of hydroxyl and hydrogen groupings on antimony oxide. No investigation of the effect of variation of oxygen content appears to have been reported other than those of Holmqvist[29] and of Kauko and Knappsberg.[13] From equation (13) the plot of emf against $\log_{10} P_{O_2}$ at constant pH should have a slope of 2·3 $RT/4F$, which Kauko and Knappsberg claim for polished antimony electrodes at pH 5·9, 7 and 9 in phosphate and borate buffers over the partial pressure range of 3–100% of oxygen. Holmqvist found an S-shaped plot with the potential of the antimony electrode changing rapidly at about 10% of oxygen and reaching constancy at high and low levels.

Results

Effect of buffers: The present work was done at pH 7 in 0·03*M* potassium chloride, with or without the addition of ammonium acetate or a phosphate buffer, and subjected to manyfold replication. Typical results are shown in Fig. 2 and support Holmqvist. Notable is the effect of buffers in shifting the potentials to more negative values and in diminishing the potential swing for a given change in oxygen pressure. The concentration of buffering substance in the solution is not critical, provided that it exceeds a minimum value of about 0·005*M*: determinations have been made in concentrations up to 0·3*M* without revealing any concentration-dependent effect. The reproducibility of the slopes is not good, but the slope $\partial E/\partial \log_{10} P_{O_2}$ in buffered solutions tends to be less than in unpoised solution. Freshly cut electrodes give lower slopes and more negative potentials than oxidized electrodes.

Equilibration time: Kauko and Knappsberg attribute Holmqvist's results to failure to attain equilibrium; and certainly equilibration is sluggish, especially at oxygen partial pressures below 10%. Accordingly, two oxygen levels falling on the straight portion between 0·5% and 10% oxygen of the emf–$\log_{10} P_{O_2}$ plot were selected, and the potential at each pressure was recorded for 6 hr repeatedly. After the initial rapid drift for 10 min, and a slow drift for a further 20 min, the potentials varied by no more than 0·25 mv. The slopes calculated from these measurements in ammonium acetate, assuming linearity of the plot, were 30 mv for freshly sawn electrodes and 57 mv for oxidised electrodes, each of these being means of three separate determinations showing a maximum scatter of 3 mv.

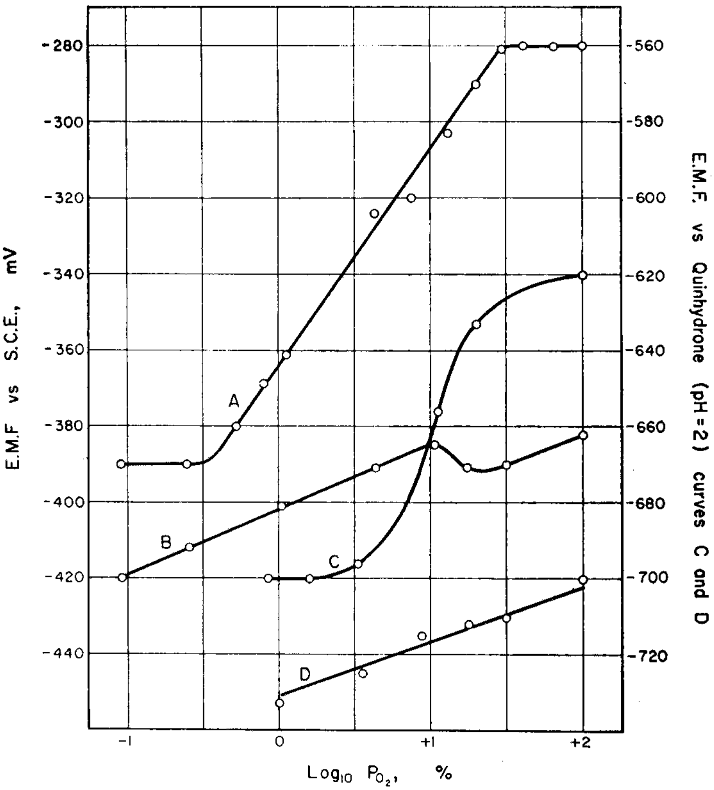


FIG. 2.—Variation of partial pressure of oxygen at pH 7.

Curve A: Unpoised solution, 0·03*M* KCl.
Curve B: Phosphate buffer.
Curve C: From Holmqvist's data.
Curve D: From Kauko and Knappsberg's data.

Discussion

The approach to constant potential at low oxygen levels can be explained by postulating either that this represents the residual partial pressure of oxygen in "white spot" nitrogen, probably about 0·1 %; or that this level represents the "failure point" of the electrode response,[16,30] *i.e.*, the concentration below which no further change in potential occurs with change in concentration of the reactive species. Constancy of potential at high oxygen levels is not so easily explained. Possibly in this region the antimony surface is fully populated with oxygen doublets, so that further increase in oxygen partial pressure does not change the potential,[31] a view in accord with the postulate of Tourky *et al.*[17,20] that antimony electrode behaviour is governed by a layer of chemisorbed oxygen on the metal surface.

The disaccord of Kauko and Knappsberg's results may be resolved on the basis of the presence of phosphate in their solutions. Electrode surfaces, even if initially dull and thickly coated with oxide, become bright and shiny after immersion in solutions containing phosphate ion. Phosphate ion evidently reacts with antimony oxide species, probably to form a phosphate antimonate-III ion, though no report of such a reaction has been traced in the literature. The measurements in phosphate media provide emf–$\log_{10}P_{O_2}$ slopes closest to the theoretical value claimed by Kauko and Knappsberg, and indicate participation of the bare metal surface in reaction (13).

The slopes of the emf–$\log_{10}P_{O_2}$ plots vary from 20 to 60 mv depending on whether electrodes are fresh or aged, and whether or not buffering substances or phosphate ion are present, forcing the conclusion that the precise involvement of oxygen in the electrode reaction is condition-dependent. Processes involving one, two or four [reaction (13)] electrons per oxygen molecule can be written:

$$2H^+ + 2Sb + 2O_2 + 2\varepsilon \rightleftharpoons Sb_2O_3 + H_2O \tag{14}$$

with a slope of

$$\frac{\partial E}{\partial(\log_{10}P_{O_2})_{T,pH}} = \frac{2{\cdot}3RT}{F};$$

$$6H^+ + 2Sb + 3O_2 + 6\varepsilon \rightleftharpoons Sb_2O_3 + 3H_2O \tag{15}$$

with a slope of

$$\frac{\partial E}{\partial(\log_{10}P_{O_2})_{T,pH}} = \frac{2{\cdot}3RT}{2F};$$

but reactions involving three electrons are less plausibly formulated:

$$18H^+ + 2Sb + 6O_2 + 18\varepsilon \rightleftharpoons Sb_2O_3 + 9H_2O$$

with a slope of

$$\frac{\partial E}{\partial(\log_{10}P_{O_2})_{T,pH}} = \frac{2{\cdot}3RT}{3F}.$$

Values of the oxygen response slopes can be accounted for on a basis of such a reaction series, one or other reaction preponderating as conditions change.

CONCLUSIONS

When used merely as an indicator electrode for locating titrimetric end-points, the antimony electrode performs satisfactorily, provided that it is not exposed to solutions outside the pH range 2–10, or solutions containing ligands that will combine with, or metal ions displaceable by, antimony; but reproducible results will be accessible only if all conditions are rigorously standardised.

The formal potential E_0', and electrode slope, are dependent on the oxygen content of the solution, the presence or absence of buffering material and the condition of the electrode surface. The oxygen response also depends on the same factors, and is markedly affected by the presence of phosphate. For the determination of pH, the response is so much dependent on conditions that the electrodes should be calibrated and used under as nearly identical conditions as possible.

The method of preparation and handling which has been described gives electrodes of excellent reproducibility independent of electrode area; but the simple mechanism of metal-metal oxide electrodes is inadequate to describe their behaviour. It seems likely that equilibrium (12) combined with (13), (14) and (15), in the presence of oxygen, is responsible for the mixed behaviour of antimony electrodes, but the marked influence of buffering materials is difficult to explain.

Acknowledgements—We thank Electronic Instruments Ltd. for the loan of instruments and support of this work, and the Cambridge Instrument Company for the loan of instruments, and one of us (G. D. S.) is indebted to Electronic Instruments Ltd. and to the Company of Scientific Instrument Makers for maintanence grants during his tenure of the E.I.L. Fellowship.

Zusammenfassung—Herstellung und Handhabung von gut reproduzierbaren Antimonelektroden genau definierter Fläche und Bestimmung der Potential-p_H-und Potential-log p_{O_2}-Beziehungen unter definierten Bedingungen werden beschrieben. Die das Ansprechen beeinflussenden Parameter werden definiert und kritisch untersucht: Reinheit, Vorgeschichte der Elektrode, Temperatur, Rührung, Ionenstärke und Zusammensetzung der Lösung, p_H, Oberflächenzustand der Elektrode und Sauerstoffgehalt der Lösung. Nachdruck wird gelegt auf den starken Einfluß von Puffern, des Oberflächenzustandes der Elektrode und des Sauerstoffgehalts der Lösung. Phosphate verändern die Oberfläche der Elektrode. Eine Ubersicht über das Verhalten bei Stromfluß wird gegeben und Elektrodenmechanismen diskutiert.

Résumé—On décrit des méthodes de préparation et de manipulation des électrodes d'antimoine, de surface précise et de bonne reproductibilité, et des méthodes de mesures potentiométriques du pH et des relations potentiel-log P_{O_2} dans des conditions controles. Les facteurs susceptibles d'affecter les caractéristiques de la réponse ont été définis et étudiés: ils comprennent la pureté de l'antimoine, les antécédents de l'électrode, la température, l'agitation, l'équilibration, la force ionique et la composition de la solution, le domaine de pH utilisé, les conditions de surface de l'électrode et la teneur en oxygéne de la solution. L'influence déterminante qu'ont les facteurs suivants: présence de tampons, conditions de surface de l'électrode et teneur en oxygéne de la solution, a été mise en lumiére. Les phosphates perturbent la surface de l'électrode. Les théories actuelles et le mécanisme des électrodes sont résumés dans le contexte de cet article.

REFERENCES

[1] E. Bishop and G. D. Short, *Analyst*, 1962, **87**, 467; and in press.
[2] G. D. Short and E. Bishop, *ibid.*, 1962, **87**, 724, 860; and in press.
[3] G. D. Short, *Current-potential relationships at antimony electrodes*, University of Exeter, 1963.
[4] M. L. Moss, J. H. Elliott and R. T. Hall, *Analyt. Chem.*, 1948, **20**, 784; J. Radell and E. T. Donahue, *ibid.*, 1954, **26**, 590; J. A. Riddick, *ibid.*, 1956, **28**, 679; J. T. Stock and W. C. Purdy, *Chem. Rev.*, 1957, **57**, 1159.
[5] G. Mattock, *pH measurement and titration*. Heywood and Co., London, 1961.
[6] D. J. G. Ives, in D. J. G. Ives and G. J. Janz, *Reference electrodes*. Academic Press, New York and London, 1961, pp. 336–351.
[7] G. Mattock, private communication, 1962.
[8] E. Bishop and J. R. B. Sutton, *Analyt. Chim. Acta*, 1960, **22**, 590.
[9] O. Gatty and E. C. R. Spooner, *The electrode potential behaviour of corroding metals in aqueous solution.* Oxford University Press, London and New York, 1938.
[10] A. M. Azzam, J. O'M. Bockris, B. Conway and H. Rosenberg, *Trans. Faraday. Soc.*, 1950, **46**, 918.

[11] A. Sovova, *Coll. Czech. Chem. Comm.*, 1963, **28**, 739.
[12] E. P. Schoch and D. G. Brown, *Trans. Amer. Electrochem. Soc.*, 1913, **22**, 265; *J. Amer. Chem. Soc.*, 1916, **38**, 1660.
[13] Y. Kauko and L. Knappsberg, *Z. Elektrochem.*, 1939, **45**, 760.
[14] G. Perley, *Ind. Eng. Chem., Analyt.*, 1939, **11**, 319.
[15] I. M. Kolthoff and B. D. Hartong, *Rec. Trav. chim.*, 1925, **44**, 113.
[16] E. Bishop and R. G. Dhaneshwar, *Analyst*, 1963, **88**, 424, 433.
[17] A. R. Tourky and E. M. Khairy, *J. Chem. Soc.*, 1952, 2626.
[18] K. Fischbeck and F. Einer, *Z. Elektrochem.*, 1938, **44**, 845.
[19] U. R. Evans, *J. Electrochem. Soc.*, 1956, **103**, 73.
[20] A. R. Tourky and A. R. Moussa, *J. Chem. Soc.*, 1948, 752.
[21] A. Kirrmann and N. Daune-Dubois, *Compt. rend.*, 1953, **236**, 1361.
[22] J. T. Stock and W. C. Purdy, *Chemist Analyst*, 1958, **47**, 36.
[23] H. T. S. Britton, *Hydrogen Ions*, Vol. 1. Chapman and Hall, London, 4th Ed., 1955.
[24] E. Bishop, *Analyst*, 1952, **77**, 672.
[25] S. E. S. El Wakkad and A. Hickling, *J. Chem. Soc.*, 1950, 2894.
[26] A. L. Pitman, M. J. N. Pourbaix and N. de Zoubov, *Trans. Electrochem. Soc.*, 1957, **104**, 595.
[27] D. N. Mehta and S. K. K. Jatkar, *J. Indian Inst. Sci.*, 1935, **18A**, 85.
[28] E. J. Roberts and F. Fenwick, *J. Amer. Chem. Soc.*, 1928, **50**, 2123.
[29] A. Holmqvist, *Undersökningar av antimous och vismuts elektromotoviska förhollanden i vattenlös-n-ingar.* Univeristy of Lund, 1936.
[30] G. Mattock, *Analyst*, 1962, **87**, 930; G. Mattock and R. Uncles, *ibid.*, 1962, **87**, 977.
[31] I. M. Issa, H. Khalifa and S. A. Awad, *J. Indian Chem. Soc.*, 1957, **34**, 275.

Talanta, 1964, Vol. 11, pp. 405 to 414. Pergamon Press Ltd. Printed in Northern Ireland

THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS OF EUROPIUM^{III} OXALATE AND SOME EUROPIUM^{II} SALTS*

A. GLASNER, E. LEVY, M. STEINBERG and W. BODENHEIMER
Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel

(*Received* 24 *June* 1963. *Accepted* 26 *September* 1963).

Summary—The differential thermal analysis curves of $Eu_2(C_2O_4)_3$, EuC_2O_4 and $EuCO_3$ exhibit prominent exothermic peaks in the region of 420° because of the oxidation of europium^{II} to europium^{III}. The first step in the decomposition of $Eu_2(C_2O_4)_3$, after completion of dehydration, is $Eu_2(C_2O_4)_3 \rightarrow 2EuC_2O_4 + 2CO_2$. The reasons for some conflicting differential thermal analysis curves of the rare earth oxalates obtained by various authors are explained. The europium^{II} oxalate, $EuC_2O_4{\cdot}1.7H_2O$, is prepared.

INTRODUCTION

THE oxalates of the rare earths are of special importance for the separation and quantitative analysis of this group of elements. There is also a wide interest in other aspects of the rare earth oxalates, as evidenced by the numerous investigations on their thermal behaviour published during the last decade. Mostly thermogravimetric (TG)[1] and differential thermal analytical (DTA)[2] methods have been employed, but the thermal curves obtained were complicated and their interpretation was often dubious.

In a series of studies carried out in this laboratory[3] the mechanism and stepwise decomposition of many of the rare earth oxalates has been elucidated by analysing the solid residues and the gaseous products formed in vacuum or in various atmospheres.[4] It was found that $Eu_2(C_2O_4)_3$[4] and $Yb_2(C_2O_4)_3$[4] were internally reduced to the bivalent cation in the first step of their decomposition, at about 300° and 340°, respectively. In the presence of oxygen the cations were soon re-oxidised to the tervalent state. In vacuum or in an inert atmosphere, bivalent carbonates (or oxycarbonates) were found to be stable well above 400°. In the light of these results a re-examination of the TG and DTA curves of $Eu_2(C_2O_4)_3$ was thought to be desirable. A few bivalent europium salts, such as EuC_2O_4, $EuCO_3$ and $EuSO_4$, were also prepared and their thermal curves were compared to that of the tervalent europium salts. Disregarding minor fluctuations, the recorded thermal curves were found to be consistent with the previously proposed mechanisms of decomposition.

EXPERIMENTAL

Reagents

Eu_2O_3 (Lindsay, code 1013, 99·9% purity) served as the starting material for all of the preparations examined in this work.

$Eu_2Ox_3{\cdot}5.8H_2O$ (or 10 *H_2O*): Prepared in the usual manner by precipitation with oxalic acid from a nitric acid solution[4] and kept in an evacuated desiccator over phosphorus pentoxide.

---

* This paper contains part of the Ph.D. thesis submitted to the Senate of the Hebrew University by E. L.

$EuSO_4$ and $EuCO_3$: Prepared as described by Cooly and Yost;[5] the solution from the Jones' reductor was allowed to pass directly into a 4*M* sulphuric acid solution and the precipitated $EuSO_4$ was filtered, washed and dried.

A batch of $EuSO_4$ was further digested in a 10% sodium hydroxide plus sodium carbonate mixture to yield the greenish-yellow $EuCO_3$, which, after drying, was found by analysis to conform to the formula $EuCO_3 \cdot 0.21H_2O$. The infrared absorption spectrum of this preparation, by the potassium bromide disc method, is shown in Fig. 1.

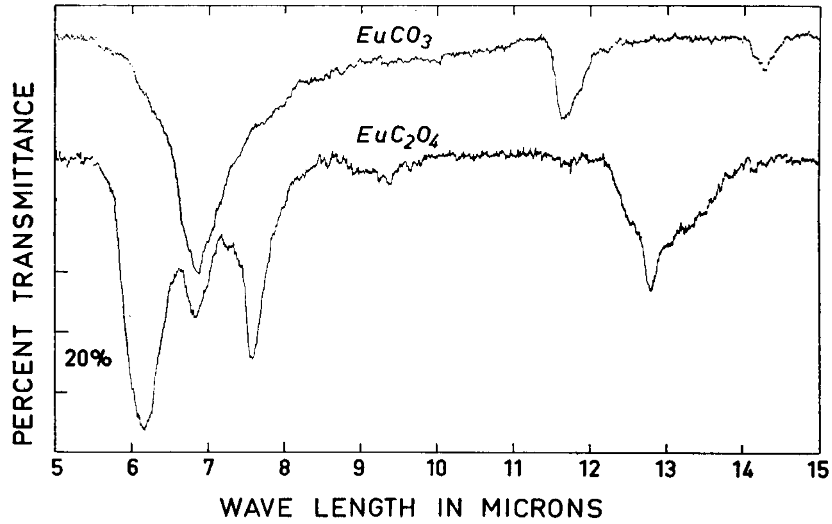


FIG. 1.—Infrared spectra of EuC_2O_4 and $EuCO_3$ showing absorption bands characteristic for the anions.

EuC_2O_4: Its preparation has not yet been described in the literature. Various procedures were investigated. On either adding the reduced solution from the Jones' reductor to a saturated solution of oxalic acid (previously boiled to expel oxygen) or dissolving $EuCO_3$ in 1*M* hydrochloric acid and adding the oxalic acid to this solution, a beige coloured precipitate was obtained. An elementary analysis* of the last preparation gave:

	Found	Theoretical		
		EuC_2O_4	$EuC_2O_4 \cdot 0 \cdot 5H_2C_2O_4$	$Eu_2(C_2O_4)_3$
C, %	13·08	10·0	12·64	12·68
H, %	0·18	0·0	0·315	0·00

and its composition is evidently undefined.

Pouring a saturated oxalic acid solution onto the solid $EuCO_3$ proved more successful. Evolution of carbon dioxide, but no dissolution of the solid (which turned from yellow to a rusty red) was observed. At this stage two volumes of distilled ethyl alcohol were added, and the red crystals were filtered and dried at 90°. If no alcohol is added, the red crystals change slowly to the beige modification, but no similar change occurs when the dry material is contacted with water. The elementary analysis of the red preparation gave 8·86% of carbon and 1·28% of hydrogen. Assuming that all hydrogen is from absorbed water or from water of crystallisation, the formula for the preparation should be $EuC_2O_4 \cdot 1 \cdot 72H_2O$, in excellent agreement with the 8·86% of carbon found. This formula was

---

* For which we are grateful to Mrs. M. Goldstein of the Organic Chemistry Department of the Hebrew University.

further confirmed by igniting a weighed portion of the preparation in air at 1000°:

	H, %	C, %	Wt. loss at 1000°, %
Theoretical for			
$EuC_2O_4 \cdot 1{\cdot}7H_2O$	(1·28)	8·86	35·0 (Eu_2O_3)
Found	1·28	8·86	34·5

The infrared absorption spectrum of this preparation, obtained by the potassium bromide disc method, is shown in Fig. 1.

$Eu_2(SO_4)_3 \cdot nH_2O$: Crystallised from a sulphuric acid solution of Eu_2O_3 by evaporation. It was collected on a fritted glass crucible and washed with a small amount of water and dry acetone. This product was not analysed, and it is therefore possible only to estimate its water content or surplus sulphuric acid, from the thermogravimetric curve.

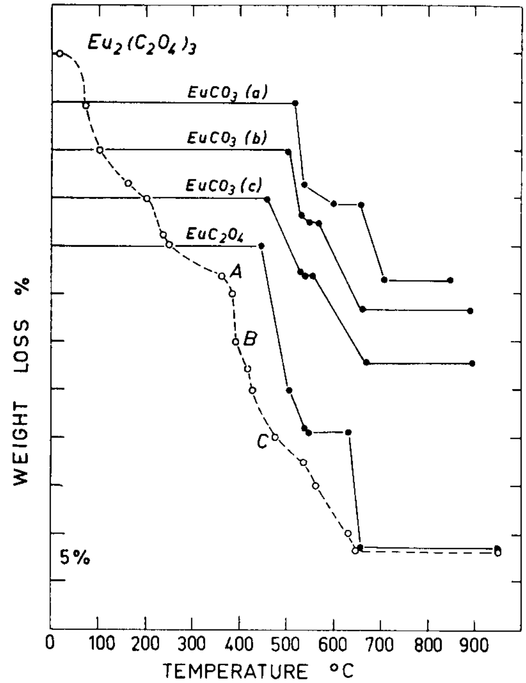


FIG. 2.—Thermogravimetric curves of $Eu_2(C_2O_4)_3 \cdot 10H_2O$, $EuC_2O_4 \cdot 1{\cdot}7H_2O$, two samples of $EuCO_3$ (a and b), and $EuCO_3$ mixed with alumina (c).

Apparatus

For the thermogravimetric measurements a Stanton decimilligram model thermobalance was used. The heating rate was maintained at 6°/min and the furnace temperature control is generally correct within ±2°. Samples weighing 100 mg each were taken for all of the experiments, so that weight losses can be directly read on the recorded thermograms in percentages.

For the DTA measurements a Gallenkamp tube furnace, provided with a ceramic heating block and ceramic twin crucibles, was employed. One of the crucibles contained the sample, mostly weighing 500 mg, mixed with an equal weight of α-alumina (previously ignited at 1000°), and the other crucible 1 g of the pure inert reference material. The rate of heating was maintained at 10°/min. Temperatures were measured with chromel-alumel thermocouples. The temperature of the alumina was taken as reference and recorded on a Kent multilec instrument, whilst the temperature difference between the two crucibles was recorded on a Kent microvolt instrument.

RESULTS

Fig. 2 shows the percentage weight loss (TG curves) obtained on heating $Eu_2(C_2O_4)_3$, EuC_2O_4 and $EuCO_3$ and Figs. 3, 4 and 5 the thermal spectra (DTA curves) of the same materials.

Europium^{III} *oxalate.* There are no distinct plateaux on the thermogram of the tervalent hydrated oxalate (Fig. 2), but one may attribute definite compositions to the decomposing sample at most points of inflection. Thus the percentage loss at *A* (350°) corresponds to the anhydrous salt $Eu(C_2O_4)_3$, the decomposition of which has been retarded by the presence of the last traces of water. The steep slope to *B* (390°) corresponds approximately to the formation of EuC_2O_4, although a partial re-oxidation of the europium by air may have taken place. Re-oxidation and decomposition of the oxalate to carbonate is completed at *C* (475°), where the weight loss indicates the composition: $(EuCO_3)_2O$. The decomposition to the sesquioxide is completed at about 650°.

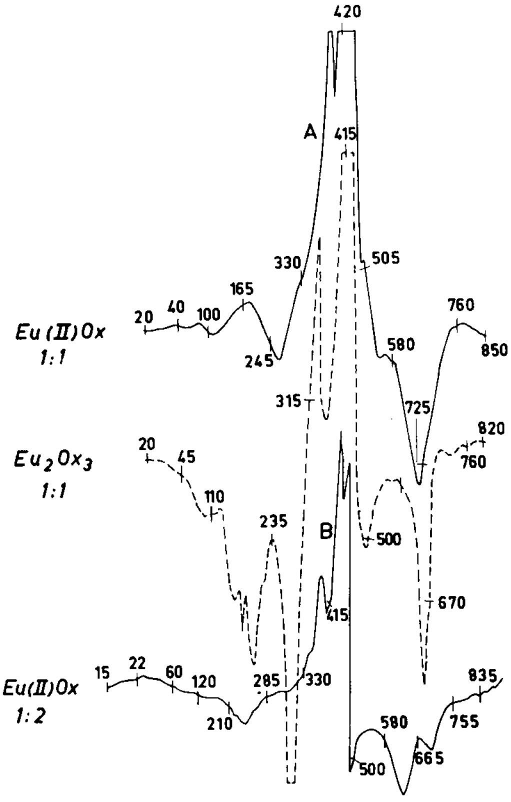


FIG. 3.—DTA curves of $Eu_2(C_2O_4)_3{\cdot}5{\cdot}8H_2O$ and $EuC_2O_4{\cdot}1{\cdot}7H_2O$. Weight ratio of oxalate to alumina for curve B was 1 : 2. Numbers on curves indicate temperatures (°C).

The most prominent feature of the DTA curves in Figs. 3 and 4 (inclusive of the $EuCO_3$ curves) is a broad and high exothermic peak at 410°–420°. For the sake of comparison, the thermal spectrum of $La_2(C_2O_4)_3{\cdot}10H_2O$ is also shown in Fig. 5, with

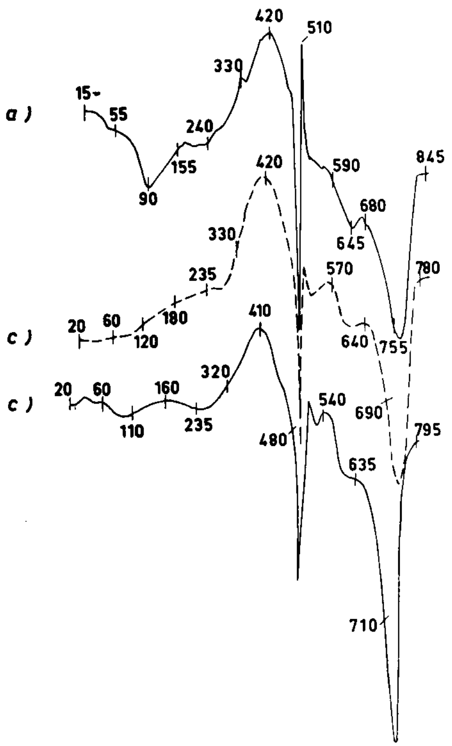


FIG. 4.—DTA curves of $EuCO_3 \cdot 0 \cdot 2H_2O$ (a), and $EuCO_3 \cdot 0 \cdot 04H_2O$ (c).

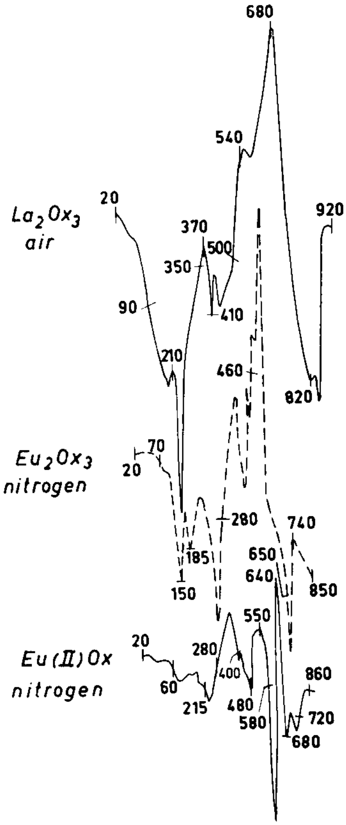


FIG. 5.—DTA curves of $La_2(C_2O_4)_3 \cdot 10H_2O$ in air, and of europium^{II} and europium^{III} oxalates in an atmosphere of nitrogen.

endothermic reactions in this range of temperatures and a prominent exothermic peak at 680°, in good agreement with the measurements of Wendlandt *et al.*[2] Hence the exothermic peaks at 420°, common to the bivalent and tervalent europium salts, are most probably from the air-oxidation of the europium, and imply a previous reduction of the tervalent europium according to the equation

$$Eu_2(C_2O_4)_3 \rightarrow 2\ EuC_2O_4 + 2\ CO_2 \qquad (1)$$

This reduction took place at a lower temperature, as indicated by the endothermic peak at ~300°.

The complete interpretation of the DTA curve of $Eu_2(C_2O_4)_3 \cdot 5 \cdot 8\ H_2O$ is therefore as follows. The endothermic peaks below 235° are from partial dehydration. The peak at about 300° is a combined effect of the final dehydration and decomposition (reduction) according to equation (1). The latter endothermic peak terminates in a narrow pointed exothermic peak because of some re-oxidation of the europium, and is soon followed by the main exothermic peak at 415° (the pointed head of this peak came beyond the limits of the paper), which hides most of the endothermic effect from the conversion of the oxalate to a carbonate

$$2EuC_2O_4 + 0 \cdot 5O_2 \rightarrow (EuCO_3)_2O + 2CO \qquad (2)$$

Reaction (2) terminates in a small endothermic peak at 490° in good agreement with the point *C* on the TG curve. The last endothermic peak at about 660° also corresponds to the formation of the oxide Eu_2O_3 indicated by the TG measurement. Some of the more prominent thermal data obtained from the TG and DTA curves are recorded in Table I for the sake of ease of comparison. The heading of each column shows the composition of the residue formed at the temperature indicated.

Table I.—Temperatures of formation

Sample	System	$Eu_2(C_2O_4)_3$	EuC_2O_4	$Eu(CO_3)_2O$	$(EuO)_2CO_3$	Eu_2O_3
$Eu_2(C_2O_4)_3\cdot10H_2O$	TG	350°	390°	475°	—	650°
$Eu_2(C_2O_4)_3\cdot5{\cdot}8H_2O$	DTA	~250°	300°	490°	—	660°
$EuC_2O_4\cdot1{\cdot}7H_2O$	TG	—	450°	550°	—	660°
	DTA	—	270°	545°	—	700°
$EuCO_3\cdot0{\cdot}21H_2O$	TG	—	—	—	>540°	>665°
	DTA	—	—	—	500°	750°
	Vacuum[a]	—	—	—	400°	620°

[a] After heating at constant temperature for 24 hr.

Europium^{II} *oxalate.* The similarity between the DTA curves of the two europium oxalates (Fig. 3) above 310° is most striking, precluding any doubts with respect to the assumed reduction of $Eu_2(C_2O_4)_3$ to EuC_2O_4 [reaction (1)] at a temperature below 310°. The endothermic peak on the EuC_2O_4 curve at ~270° is from dehydration (1·7 MH_2O per formula weight), but we have no explanation for the small exothermic peak at ~180°.

Fig. 3, curve *B*, shows another DTA run with EuC_2O_4 and α-alumina mixed in the weight ratio of 1:2. As expected, the thermal effects are less pronounced, but better resolved in this case; three exothermic peaks are followed by three endothermic peaks, all at temperatures corresponding to those which may also be observed on curve *A* with the 1:1 mixture.

Two more DTA curves, one of EuC_2O_4 and one of $Eu_2(C_2O_4)_3$, obtained on passing a current of nitrogen through the cylinder which contained the double crucible, are shown in Fig. 5. The exothermic peaks were not eliminated in these experiments, but they were shifted to considerably higher temperatures. In other aspects the two thermal spectra are similar to the two corresponding curves obtained in air (Fig. 3). Hence it may be inferred that under conditions of limited access of oxygen, the exothermic oxidation of europium^{II} to europium^{III} is completed at 560° and at 640°, when the initial salts were $Eu_2(C_2O_4)_3\cdot5{\cdot}8H_2O$ and $EuC_2O_4\cdot1{\cdot}7H_2O$, respectively.

On the thermogram of EuC_2O_4 (Fig. 2), no change of weight corresponding to the DTA peaks up to 420° was observed. (Apparently the alumina admixed with the sample in the DTA experiments assists dehydration and consequently promotes the whole sequence of the decomposition reactions.) Decomposition starts at 450°, with a steep loss of weight (19·5%). The plateau between 550° and 630° indicates the stability of the intermediate oxycarbonate $(EuCO_3)_2O$, which again decomposes in one step to the oxide Eu_2O_3. The agreement between the latter half of the TG and the DTA curves is good.

Europium^{II} *carbonate.* Three thermograms of the decomposition of $EuCO_3$ are shown (Fig. 2): (a) the analysed sample which contained 0·21 M H_2O per formula weight, (b) another preparation which contained only about 0·04 M H_2O, and (c) a sample of the latter preparation admixed with an equal weight of alumina, as in the DTA experiments. In all three cases decomposition occurred in two steps, as shown in detail in Table II.

TABLE II.—COMPILED DATA OF TG RUNS ON $EuCO_3$

	Temp. range of 1st step, °*C*	Wt. loss for $(EuO)_2CO_3$, %		Temp. range of 2nd step, °*C*	Wt. loss for Eu_2O_3, %	
		Calc.	Found		Calc.	Found
a	520–605	8·3	10·5	665–715	18·5	18·4
b	505–550	6·9	7·5	570–665	17·1	16·6
c	455–540	6·9	8·0	555–675	17·1	17·0

The final weight loss indicates in all three runs the formation of Eu_2O_3 at about 700°. On the other hand, the loss at the intermediate stage is always larger than that calculated for $(EuO)_2CO_3$. This difference suggests that the bivalent europium has been only partially oxidised to the tervalent state (complete oxidation gives a *gain* in weight of 3·7%).

It is of interest to note the lowering of the temperature of the initial decomposition in sample *b*, containing less water, and again in run *c*, where the admixed alumina assists dehydration.

On the DTA curve (Fig. 4) of sample *a* one can actually observe the endothermic dehydration peak at 95°, which is absent on the two parallel runs of sample *c*. The parallel runs exemplify the excellent reproducibility of these analyses. The prominent exothermic peaks at 410°–420°, which testify to the oxidation of the europium, occur at the very same temperature as those on the DTA curves of the oxalates. The absence of parallel changes of weight on the TG curve (Fig. 2, curve *a*) are understandable if it is assumed that alumina assists dehydration and that the dehydrated carbonate is more prone to oxidation. (In the thermogravimetric runs there may also be a partial cancellation of the loss of weight from dehydration and the weight gained by oxidation).

A pointed narrow endothermic peak at 500° shows evidence of another reaction, namely the decomposition to the oxycarbonate, proceeding simultaneously with the oxidation of the europium. The oxidation reaction is indeed completed only at 510°, as indicated by a second pointed exothermic peak. The final decomposition to the oxide was shifted to higher temperatures (750°) in the DTA experiments as compared with the TG experiments (see Table I).

It should be emphasised that on heating $EuCO_3$ at temperatures above 400°, the evolving carbon dioxide may oxidise the europium to the tervalent state, even in the absence of air. This is illustrated in Table III, which shows the composition of

TABLE III.—COMPOSITION OF GASES EVOLVED FROM $EuCO_3$ ON HEATING

Temp., °*C*	Wt. of sample, *mg*	Expected total pressure, μ	Partial pressures			
			μ (CO_2)	μ (CO)	CO_2, %	CO, %
400	3·47	62·8	15	12	23·9	19·1
620	5·33	96·5	54	41	55·9	42·5
1000	7·48	135·4	62	62	45·8	45·8

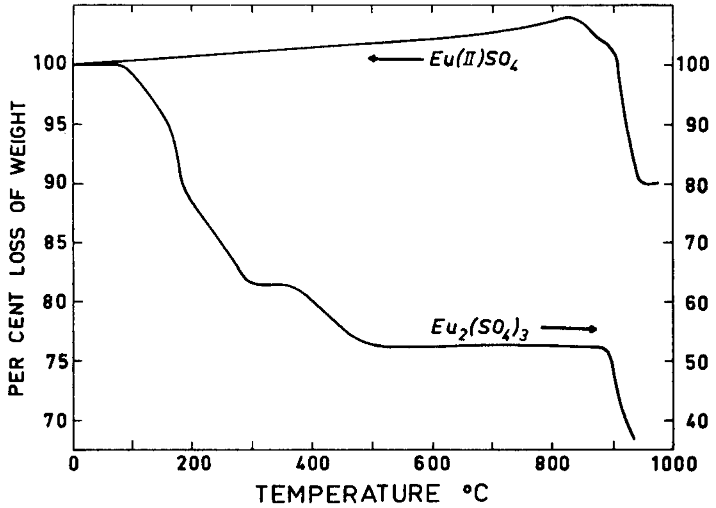


FIG. 6.—Thermogravimetric curves of europium^{II} and europium^{III} sulphates. Arrows indicate ordinate scale to be used.

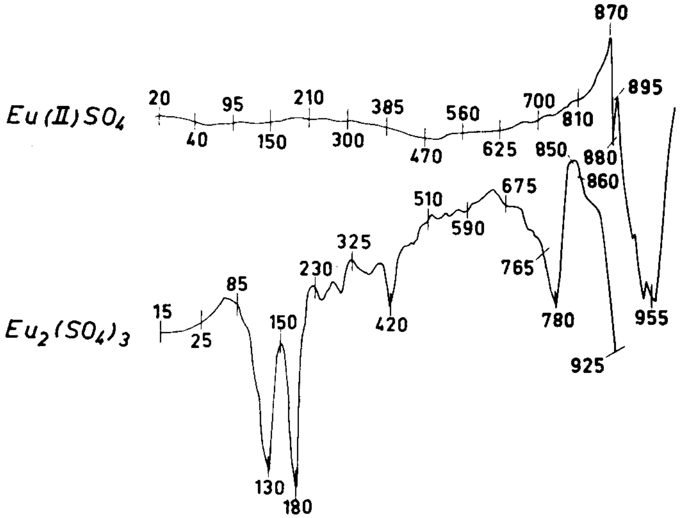


FIG. 7.—DTA curves of europium^{II} and europium^{III} sulphates.

the gases accumulated in the vacuum apparatus after heating for 24 hr at the indicated temperatures.

At 400° the residue approximates to the composition of the oxycarbonate $(EuO)_2CO_3$, while at 620° the decarbonisation is complete, but the oxidation of the europium seems to be 100% only at higher temperatures.

The TG and DTA curves of the europium sulphates are shown in Figs. 6 and 7. On the thermogravimetric curve of $EuSO_4$ the oxidation of the europium is indicated by a slow continuous increase in weight up to 830°. At this point decomposition of $(EuSO_4)_2O$ sets in, proceeding at an increased rate from 910° upwards, to form the oxysulphate $(EuO)_2SO_4$ at 950°. The oxidation peak at 870° and the endothermic peaks at 940°–960° on the DTA curve are in good agreement with this interpretation.

The thermal decomposition of $Eu_2(SO_4)_3$, among other rare earth sulphates, has been recently studied by Nathans and Wendlandt.[6] The starting points for the decomposition of the anhydrous salt indicated by our curves are: 880° (870°, TG) and 855° (810°, DTA) (the results of Nathans and Wendlandt are given in the brackets).

The dehydration of our hydrated sample proceeded in three steps, indicated by three endothermic peaks at 130°, 180° and 420°, and by the corresponding changes in the slope of the weight-loss curve.

An additional endothermic peak at 780° is inexplicable, considering the level plateau between 500° and 880° on the TG curve.

There is an intermediate plateau on the TG curve, between 300° and 360° at about 37% weight loss, which suggests the intermediate composition $Eu_2(SO_4)_3 \cdot H_2SO_4 \cdot H_2O$ and the formula $Eu_2(SO_4)_3 \cdot H_2SO_4 \cdot 24H_2O$ for the initial sample.

DISCUSSION

The DTA curves of Wendlandt *et al.* for the rare earth oxalates[2] show, as a rule, endothermic peaks in the temperature range 350°–600°, with the exception of $Eu_2(C_2O_4)_3$ which exhibits a prominent exothermic peak at 390°. In contrast, Blum and Maguire[7] obtained with the oxalates of yttrium, lanthanum, neodymium, samarium and gadolinium a series of exothermic peaks in the same range of temperatures, and stated that "the curves could be re-run with extremely good reproducibility".

Claudel, in a thesis[8] on the thermal decomposition of thorium oxalate, investigated the occasional appearance of an exothermic peak in the region of 400°, observed by Padmanabhan *et al.*,[9] but absent on the curve of Wendlandt *et al.* Claudel attributes the exothermic reaction to the air oxidation of carbon monoxide evolving from the decomposing oxalate (catalysed by thorium dioxide). He demonstrates that the oxidation is promoted by a metallic container and the use of alumina (absorbed oxygen) as the inert diluent, while in an atmosphere of nitrogen only an endothermic peak was obtained under any condition. Hence, it seems plausible that Blum and Maguire's experiments were carried out under exceptionally good oxidising conditions.

A comparison of the $La_2(C_2O_4)_3$ curves shows that our experimental conditions were very much the same as those of Wendlandt *et al.*, the exothermic peak from the oxidation of carbon monoxide or deposited carbon, appearing at 680° (Fig. 5). The same curve is reproduced on flushing the apparatus with nitrogen, and it is supposed that the oxygen adsorbed on the alumina serves as oxidant in this case.

It is interesting to note that, particularly in the case of $La_2(C_2O_4)_3$, there is no exothermic, but a broad shallow endothermic peak in the region of 700° on Blum and Maguire's DTA curve. Evidently, all carbon monoxide and carbon has been burned away below 600°.

Attribution of the prominent exothermic peaks at 420° on the thermograms of the salts of europium to the oxidation of europium^{II} to europium^{III} is, therefore, the only straightforward conclusion to the above considerations. In the case of $Eu_2(C_2O_4)_3$, reaction (1) obviously precedes all other reactions in the consecutive steps of decomposition,[4] and hence the great similarity between the thermograms of the europium^{II} and europium^{III} oxalates above 400°.

By flushing the DTA chamber with nitrogen, the oxidation of europium^{II} to europium^{III} could not be prevented, but it proceeded at a slower rate and was shifted to higher temperatures. The probable source of oxygen in this case was the gas adsorbed by the bulky alumina powder, yet the infiltration of some air with the stream of nitrogen cannot be excluded. The oxidation of europium^{II} in $EuSO_4$ is rather slow, and the exothermic peak on the DTA curve appears only at 870°. On the TG curve, on the other hand, the continuous gain in weight is clearly discernable. Hence, the proneness of the europium^{II} salts to oxidation appears to be in the following increasing order: $EuSO_4 < EuC_2O_4 < EuCO_3 < EuO$.

In conclusion, it should be remarked that DTA curves may supply useful information only in conjunction with data from other methods of investigation. Unexpected complications that might arise are well exemplified in the case of the oxalates. In a well aerated apparatus the evolving carbon monoxide may be oxidised at a comparatively low temperature (~400°),[4] but the sample will overheat only if the oxidation takes place in the bulk of the material. With a limited supply of oxygen disproportionation occurs and the exothermic peak is shifted to a temperature above 600°, when the deposited carbon burns away. The exothermic peak from the oxidation of europium^{II}, on the other hand, is not subject to such irregularities.

Zusammenfassung—Die DTA-Kurven von $Eu_2(C_2O_4)_3$, EuC_2O_4 und $EuCO_3$ zeigen um 420° deutliche exotherme maxima, die auf Oxydation von Europium^{II} zu Europium^{III} beruhen. Die erste Stufe der Zersetzung von $Eu_2(C_2O_4)_3$ nach beendeter Entwässerung wird durch die Gleichung $Eu_2(C_2O_4)_3 \rightarrow 2EuC_2O_4 + 2CO_2$ beschrieben. Gründe für nicht übereinstimmende DTA-Kurven der Oxalate seltener Erden von verschiedenen Autoren werden angegeben. Ein Europium^{II}-oxalat mit $1{\cdot}7H_2O$ wurde dargestellt.

Résumé—Les courbes DTA des systèmes $[Eu^{(III)}]_2Ox_3$, $[Eu^{(II)}]Ox$ et $[Eu^{(II)}]CO_3$ présentent des pics exathermiques importants dans la région des 420°C, dûs à l'oxydation de l'ion europeux en ion europique. La première étape de la décomposition de Eu_2Ox_3 après deshydration complète est donnée par l'équation

$$Eu_2Ox_3 \rightarrow 2EuOx + 2CO_2.$$

Les raisons de discordance de quelques courbes DTA d'oxalates de terres rares obtenues par différents auteurs sont éclaircies. Le préparation d'un oxalate, $[Eu^{(II)}]Ox \,.\, 1{\cdot}7H_2O$ est décrivé.

REFERENCES

[1] W. W. Wendlandt, *Analyt. Chem.*, 1958, **30**, 58; 1959, **31**, 408. Many other works are cited in the papers under reference 4.

[2] W. W. Wendlandt, T. D. George and G. R. Horton, *J. Inorg. Nuclear Chem.*, 1961, **17**, 273; E. C. Shears, *Trans. Brit. Ceram. Soc.*, 1962, **61**, 225.

[3] A. Glasner and M. Steinberg, *Bull. Res. Council Israel*, 1959, **8A**, 174; *J. Inorg. Nuclear Chem.*, 1961, **16**, 279; **22**, 39, 156.

[4] A. Glasner, E. Levy and M. Steinberg, *ibid.*, 1963, **25**, 1119, 1415, and to be submitted.

[5] R. A. Cooly and D. M. Yost, *Inorganic Synthesis.* McGraw Hill, 1946, Vol. 2, p. 70.

[6] M. W. Nathans and W. W. Wendlandt, *J. Inorg. Nuclear Chem.*, 1962, **24**, 869; W. W. Wendlandt and T. D. George, *ibid.*, 1961, **19**, 245.

[7] S. L. Blum and E. A. Maguire, *Amer. Ceram. Soc. Bull.*, 1960, **39**, 310.

[8] B. Claudel, A study of the thermal decomposition of the nitrate and the oxalate of thorium. Thesis presented to the Faculty of Science of the University of Lyon (1962).

[9] V. M. Padmanabhan, S. C. Saraiya and A. K. Sundaram, *J. Inorg. Nuclear Chem.*, 1960, **12**, 356.

Talanta, 1964, Vol. 11, pp. 415 to 422. Pergamon Press Ltd. Printed in Northern Ireland

AN INVESTIGATION OF 2-AMINO-4-CHLOROBENZENETHIOL HYDROCHLORIDE AS A SPECTROPHOTOMETRIC REAGENT FOR THE DETERMINATION OF MOLYBDENUM

GORDON F. KIRKBRIGHT and JOHN H. YOE
Pratt Trace Analysis Laboratory, Department of Chemistry, University of Virginia
Charlottesville, Virginia, U.S.A.

(*Received* 20 *June* 1963. *Accepted* 4 *August* 1963)

Summary—2-Amino-4-chlorobenzenethiol hydrochloride forms a green precipitate with molybdenum^{VI} at pH 2. The precipitate can be extracted into chloroform and has an absorbance maximum at 720 mμ. The sensitivity of the reaction is 0·0054 μg of molybdenum per cm^2 for $\log I_0/I = 0{\cdot}001$. Development of the spectrophotometric method for the determination of molybdenum included a study of the effect of pH, reagent concentration, rate of complex formation and extraction, temperature and conformity to Beer's law. The method has been applied to the determination of molybdenum in steel and cast iron.

A SYSTEMATIC qualitative investigation of the reactivity of a number of aromatic mercapto compounds with 78 inorganic ions was undertaken utilising the spot-test procedure of Yoe.[1] It was found that 2-amino-4-chlorobenzenethiol hydrochloride reacts with molybdate ions in aqueous solution over a wide range of pH to form an insoluble green complex. The precipitate can be extracted into chloroform and other non-polar and polar solvents. The variables governing formation and extraction of the complex have been studied, and a method for the spectrophotometric determination of traces of molybdenum has been developed and applied to the analysis of steel and cast iron.

PRELIMINARY QUALITATIVE STUDIES

2-Amino-4-chlorobenzenethiol hydrochloride hydrolyses in water to the free base, which is insoluble in water. The hydrochloride is quite soluble in ethanol, however, and a 1% solution in 95% ethanol was used to investigate the reactivity of the compound with metal ions.

The reagent forms colours or precipitates with a number of metal ions. Between pH 2 and 10 it forms precipitates with molybdenum (green), palladium (orange), bismuth (orange), lead (yellow), nickel (pale green), cobalt (brown), copper (pale green), tungsten (white), cadmium (white) and zinc (white). The reagent also precipitates slowly when the alcoholic solution is added to the aqueous metal ion solution. No reaction was observed between molybdenum and the reagent between pH 1 and 4 in the presence of a large amount (greater than 1000-fold excess over the molybdenum present) of EDTA, citrate, tartrate, oxalate and fluoride, although the presence of excess potassium cyanide did not affect the reaction.

The molybdenum complex can be extracted into chloroform, carbon tetrachloride, benzene, isoamyl alcohol, isopropyl ether and petroleum ether between pH 1 and 4. When freshly precipitated from aqueous solution it can also be dissolved by the addition of ethanol, methanol, acetone, isopropyl alcohol, pyridine, dioxan or dimethylformamide. The solvents used to dissolve the precipitate all produce a clear solution whose green colour fades rapidly. Of the solvents used to extract the complex, only chloroform, carbon tetrachloride and benzene produce a green organic phase whose colour is sufficiently stable for spectrophotometric measurement. Under standardised conditions for the colour formation and extraction, the absorbance spectra of the complex dissolved in these three non-polar solvents are virtually identical with respect to both the wavelength and intensity of the absorption maximum. Chloroform was chosen as the extractant, because it was preferred to use a solvent of density greater than water. The free reagent also extracts into chloroform and produces an organic phase which is yellow in colour. The intensity of the yellow colour is dependent upon the extraction pH.

The palladium and bismuth complexes of the reagent can also be extracted into chloroform, but the precipitates formed with the other metal ions mentioned previously are either insoluble in chloroform or only slightly soluble and produce a colourless organic phase.

EXPERIMENTAL

Apparatus

Spectrophotometers: Beckman Spectrophotometers, Models DU and DK-2, with matched 1-cm Corex cells.

pH meter: Beckman Model G, with general-purpose glass electrode.

Reagents

2-*Amino*-4-*chlorobenzenethiol hydrochloride:* Obtained from Eastman Kodak (No. 3279) in the form of pale yellow crystals. It is only slightly soluble in water, and was used as a 4% solution in 95% ethanol. The pale yellow solution becomes deep yellow over a period of several days and appears to undergo slow decomposition. The reagent solution was therefore prepared fresh every 2 days.

Standard molybdenum solution: 1·840 g of dry ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, ('Baker Analyzed' A.C.S.) was dissolved in distilled water and diluted to 1 litre. The solution was standardised by precipiting the molybdenum with α-benzoinoxime, igniting the precipitate and weighing as the oxide.[2] The 1000 ppm of molybdenum^{VI} standard stock solution was diluted as required.

Buffer solutions: Clark and Lubs buffers were used throughout.

Na_2H_2EDTA (*disodium salt of ethylenediaminetetra-acetic acid*): 3% aqueous solution.

Solutions of diverse ions: Reagent-grade salts were used to prepare solutions of various ions. The solutions were made to contain 1 g of the ion per litre of solution.

All other reagents were analytical reagent grade.

Preparation of calibration curves

(*a*) *Pure solution:* Transfer 0, 1·0, 2·0, 3·0, 4·0 and 5·0 ml of standard molybdenum solution (10 μg of Mo per ml) to 50-ml separating funnels. Add 3 ml of pH 2·2 buffer solution and dilute each solution to 10 ml with distilled water. Add 0·25 ml of 4% 2-amino-4-chlorobenzenethiol hydrochloride reagent solution, mix, and allow to stand for 15 min. Add 10·0 ml of chloroform and shake vigorously for 1 min. When the phases have separated, measure the absorbances at 720 mμ using a chloroform blank.

(*b*) *Steel analysis:* Transfer 0, 1·0, 2·0, 3·0, 4·0 and 5·0 ml of the standard molybdenum solution (10 μg of molybdenum per ml) to 50-ml separating funnels. Add to each funnel a volume of ferric chloride solution (10 mg/ml) which contains approximately the equivalent amount of iron to that present in the steel or cast iron sample. Add just sufficient 3% Na_2H_2EDTA solution to complex the ferric iron added, and add 5 ml of pH 2·4 buffer. Dilute each solution to the same volume with distilled water. Add 0·25 ml of 4% 2-amino-4-chlorobenzenethiol hydrochloride solution, mix, and allow to stand for 15 min. Add 10·0 ml of chloroform and shake vigorously for 1 min. Measure the absorbances of the chloroform phases at 720 mμ against a reagent blank.

Preparation of samples for analysis

Dissolve the sample (0·2–0·5 g) in a mixture of 10 ml of hydrochloric acid and 3 ml of nitric acid. Evaporate the solution to small volume, dilute with 10 ml of water and boil. Dilute the solution to 40–50 ml with distilled water, adjust the pH of the solution to 1·5–2·0 with dilute aqueous ammonia solution, transfer the solution to a 100-ml volumetric flask, and dilute to volume. Take a 1-ml aliquot of the solution for analysis, and, assuming the sample to contain 100% ferric iron, add the required volume of 3% Na_2H_2EDTA solution (0·45–1·2 ml) to complex the iron present. After the addition of the buffer and reagent, determine the molybdenum content as described for calibration curve (*b*).

The conditions, the volume of the solution, pH and time of shaking, *etc.*, should be carefully controlled in order to obtain good reproducibility.

DETERMINATION OF OPTIMUM CONDITIONS

Spectral characteristics

The absorbance spectra for 2-amino-4-chlorobenzenethiol and its molybdenum complex in chloroform are shown in Fig. 1. The molybdenum complex has a well-defined absorption maximum at 720 mμ. The reagent exhibits no absorbance at 720 mμ, and only begins to absorb appreciably at wavelengths less than 450 mμ. The 720 mμ absorbance maximum is suitable for spectrophotometric absorbance measurements and no reagent blank is required.

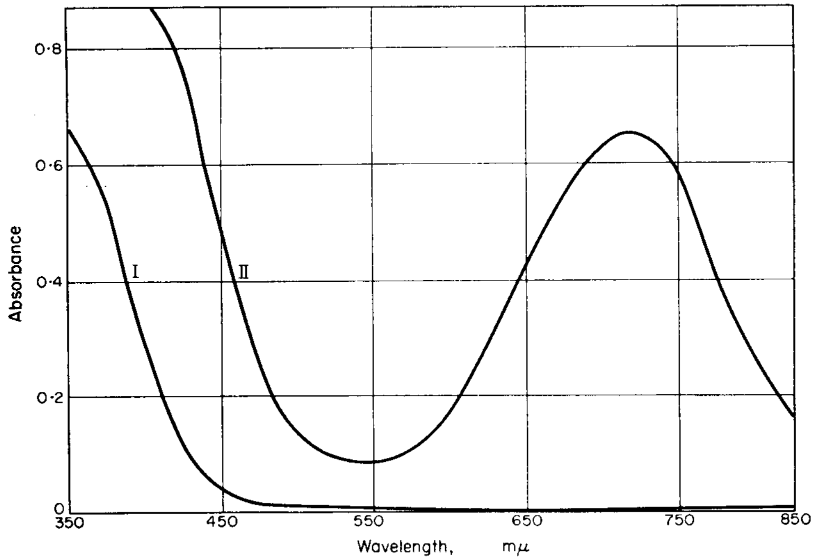


FIG. 1.—Absorbance spectra for (I) reagent and (II) molybdenum complex against chloroform at pH 2 (20 μg of Mo).

Effect of pH

(*a*) *Complex formation.* Curve (I) in Fig. 2 shows the effect of pH on the formation of the molybdenum complex in aqueous solution. A constant large excess of reagent solution was added to buffered solutions containing 20 μg of molybdenum^{VI}, and the mixture was allowed to stand for 15 min. The solutions were then brought to pH 1 by the dropwise addition of dilute hydrochloric acid, and extracted with 10 ml of chloroform for 1 min. The absorbances of the chloroform extracts were measured at 720 mμ using a chloroform blank. The optimum pH for complex formation is at 1·9–3·3.

(*b*) *Solvent extraction.* Curve II in Fig. 2 shows the effect of pH on the extraction of the molybdenum complex into chloroform. The precipitate of the complex was formed at pH 2·8 and allowed to stand for 15 min. The pH of the solutions was adjusted to between 1 and 5 by the addition of a large excess of the required buffer, and the solutions were shaken immediately with 10 ml of chloroform for 1 min. The absorbance of the chloroform extracts was measured at 720 mμ against a chloroform blank. For solvent extraction the pH of the solution should be adjusted to between 1 and 2·3. The complex can also be extracted at pH < 1, in dilute hydrochloric acid medium, and there is no significant variation in the absorbance with acid concentration when the medium is 0·1–0·3*M* with respect to hydrochloric acid. All pH values are uncorrected for ionic concentration.

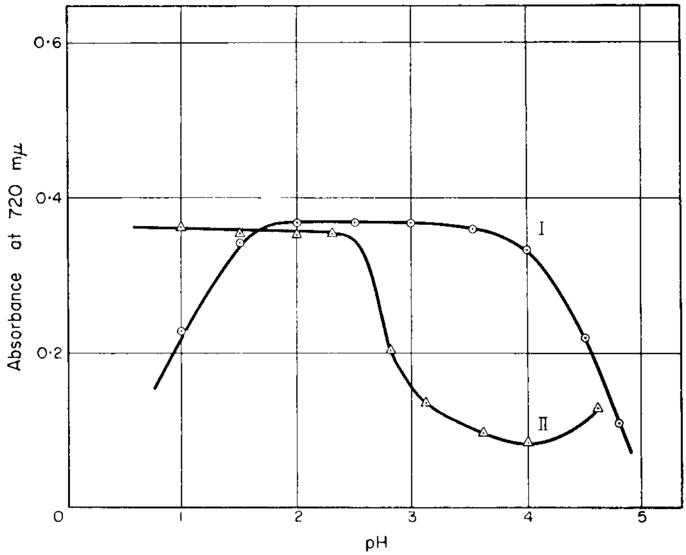


FIG. 2.—Effect of pH on absorbance at 720 mμ: (I) complex formation and (II) solvent extraction.

Order of addition of reactants

The ethanolic solution of 2-amino-4-chlorobenzenethiol must be added to the buffered molybdenum^{VI} solution. Because of the precipitation of the reagent in aqueous solution, sufficient excess of reagent does not remain in solution to give a rapid quantitative reaction if the molybdenum solution is added to the buffered reagent solution.

Effect of reagent concentration and time of shaking

It was found satisfactory to use 1 ml of a 1% reagent solution in ethanol. When the effect of the time of shaking on the absorbance at 720 mμ was studied using this reagent concentration, however, it was found that the absorbance decreased considerably when the shaking time was extended above 1 min. Further investigation revealed that the decrease was related to the volume of ethanol present, and that the rate of decrease was considerably less when a smaller volume of a more concentrated reagent solution was used. As shown in Fig. 3, when 0·25 ml of a 4% reagent solution in ethanol was used no change in absorbance was produced when the mixture was extracted between 30 and 60 sec.

Time required for complex formation

At least 5 min are required for the formation of the extractable molybdenum complex in order to obtain constant absorbance after extraction. The mixture may be allowed to stand for as long as 1 hr before extraction without change in the absorbance of the chloroform extract at 720 mμ. A 15-min standing time was adopted for convenience.

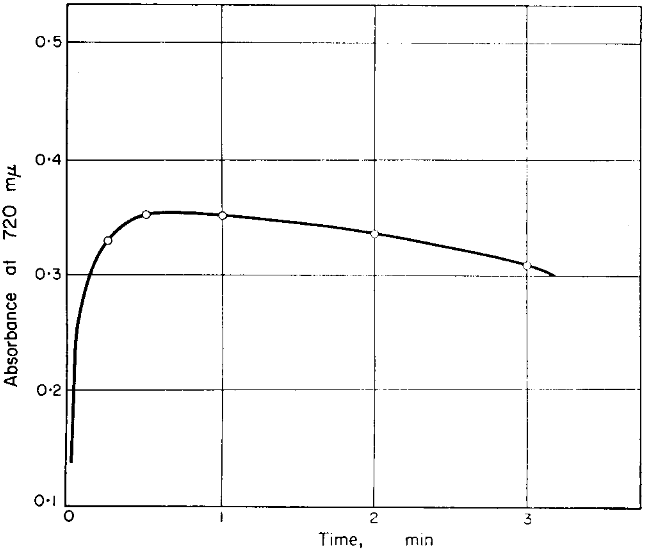


FIG. 3.—Effect of extraction time on absorbance.

Effect of temperature

The complex formation was conducted at temperatures between 10° and 40° in a water bath. No significant variation in the absorbance of the chloroform extract was observed.

Beer's law and sensitivity

The calibration curve follows Beer's law in the range 5–45 μg of molybdenum in 10 ml of chloroform. The optimum range for absorbance measurements on the spectrophotometer is 0·2–0·7 unit. With the recommended procedure these values correspond to 10–35 μg of molybdenum in 10 ml of chloroform.

According to Sandell's expression of sensitivity,[3] *i.e.*, μg of Mo per cm^2 for log $I_0/I = 0{\cdot}001$, the sensitivity was found to be 0·0054 μg of Mo per cm^2. A more practical sensitivity, however, based on an absorbance reading of 0·005 unit, is 0·027 μg of Mo per cm^2.

Stability

The absorbance of the chloroform solution of the molybdenum complex was found to decrease by 6% after standing for 4 hr and 9% after 6 hr. The absorbance should be measured at 720 mμ within 30 min after the extraction.

Precision

To obtain the precision of the method in pure molybdenum solutions, the same amount of molybdenum was determined 12 times. The average absorbance was 0·351 and the standard deviation 0·004 or 1·1%. This precision, however, is not obtained when complex mixtures are analysed. The values for the precision of three such analyses are given in Table I.

TABLE I.—ANALYSIS OF NBS SAMPLES

NBS Sample	Mo, % NBS	Mo, % Found[a]	Difference, %
72a chromium-molybdenum steel	0·202	0·199	
		0·201	
		0·197	
		0·203	
	Av.	0·200	−1·0%
Standard deviation = 0·0026 or 1·3%			
36 chromium-molybdenum steel	1·01	1·02	
		1·01	
		1·00	
		1·04	
	Av.	1·02	+1·0%
Standard deviation = 0·017 or 1·7%.			
107 nickel-chromium-molybdenum cast iron	0·687	0·678	
		0·675	
		0·670	
		0·690	
	Av.	0·678	−1·31%
Standard deviation = 0·0085 or 1·24%.			

[a] Each value represents the average of three aliquots in good agreement.

Interference studies

The preliminary qualitative investigation revealed that the most serious interfering ions in the determination of molybdenum were the transition metal ions. These ions consume the reagent and form non-extractable precipitates. Other interferences result from metal ions which are precipitated as their hydrated oxides at the recommended pH, and from certain complexing anions which interfere with the formation of the molybdenum complex.

Solutions were prepared containing 20 μg of molybdenum and varying concentrations of each ion to be tested. The molybdenum was then determined by the recommended procedure. The limiting value of the concentration of foreign ion was taken as that which caused an error of 3% in the absorbance. This corresponds to an error of 0·01 absorbance unit.

The presence of a 100-fold excess (2 mg) of the following ions caused no interference: Al^{3+}, Ba^{2+}, Ca^{2+}, Cr^{3+}, Fe^{2+}, K^+, Mg^{2+}, Mn^{2+}, NH_4^+, Na^+, Sr^{2+}, VO_2^{2+}, VO_3^-, Br^-, I^-, SO_4^{2+}, HSO_3^- and $B_4O_7^{2-}$. A 100-fold excess of the following caused the negative error given in parentheses: F^- (31%), CO_3^{2-} (12·5%), CNS^- (6·5%), acetate (7·5%), citrate (15%), oxalate (22%), phosphate (7%), silicate (15%), tartrate (13%), ascorbic acid (7%). A 100-fold excess of EDTA produced less than 3% error in the absorbance.

The following ions caused not greater than 3% error in the absorbance produced by 20 μg of molybdenum when present in the number of fold excess given in parentheses: Au^{3+} (5), As^{3+}(50), Bi^{3+} (20), Ce^{4+} (40), Co^{2+} (0·5), Cr^{6+} (2), Cu^{2+} (1), Fe^{3+} (50), Ga^{3+} (20), Ge^{2+} (35), Hg^{2+} (4), Ni^{2+} (3), Pb^{2+} (25), Pd^{2+} (2), Pt^{2+} (25), Th^{4+} (50), W^{6+} (0·5), Zn^{2+} (10).

Ag^+ is precipitated as its chloride. Se^{4+} and Te^{4+} give a yellow precipitate with the reagent which is extracted into chloroform. Ti^{4+} and Zr^{4+} are precipitated and cause negative errors.

Nature of complex

The complex was isolated as a green precipitate by the addition of a slight excess of the reagent solution to 100 ml of $10^{-2}M$ molybdate solution at pH 2. The precipitate was filtered off, washed with a mixture of 2 volumes of ethanol and 1 volume of water, and dried to constant weight at 50°. The molybdenum content was then determined by igniting a weighed portion to molybdenum trioxide at 500°. The results of the duplicate analyses were 15·9% and 16·0% of Mo. A 3:1 complex of reagent to molybdenum requires 15·8% Mo, *e.g.*, $MoO(OH).[C_6H_5NSCl]_3$.

A study was made to determine the empirical formula of the molybdenum complex in solution. The mole ratio method of Yoe and Jones[4] gave indication of a 3:1 complex of reagent to molydbenum, and the subsequent formation of a higher complex. The complex appears to be appreciably dissociated, because no sharp breaks were observed. The continuous variations method of Job,[5] as modified by Vosburgh and Cooper,[6] gave results in agreement with those obtained from the mole ratios studies and the determination of the molybdenum content of the solid complex. It seems that a 3:1 complex of reagent to molybdenum is formed and there is some indication of the existence of a higher complex.

ANALYSIS OF COMPLEX MIXTURES

The principal interferences, from a practical viewpoint, are $iron^{III}$, copper, cobalt, nickel and tungsten. The permissible concentrations of these ions, with the exception of $iron^{III}$, are high enough to allow the determination of molybdenum in a range of steel and cast iron samples. Although an appreciable excess (1 mg) of $iron^{III}$ can be tolerated, this value is too low to permit the analysis of these samples without masking or prior separation of the iron.

An attempt was made to separate the iron by precipitation as ferric hydroxide. Coprecipitation errors, even after repeated precipitation by the method recommended by Lundell and Hoffman,[7] prevented complete recovery of the molybdate. The interference from $iron^{III}$ was successfully overcome by the addition of EDTA to the sample solution. An appreciable excess of EDTA (2 mg) can be tolerated, but it was preferred to add only the required amount, calculated assuming the steel and cast iron samples contained 100% of iron. Under these conditions, high results were obtained when the sample absorbance is compared with a calibration curve obtained using pure molybdenum solutions. A calibration curve was produced from standard molybdenum solutions containing a large excess of $iron^{III}$ and the equivalent amount of Na_2H_2 EDTA. Comparison of absorbance values against this calibration curve gave better accuracy, although slightly lower precision, than when the calibration curve obtained from pure solution was used.

To test the efficiency of the method, three National Bureau of Standards samples were analysed for molybdenum. The results are shown in Table I.

Acknowledgements—We are indebted to the Pratt Trace Analysis Laboratory for the grant of a Fellowship to one of us (G. F. K.), and wish to thank Ann Kirkbright for her assistance with this work.

Zusammenfassung—2-Amino-4-chlorthiophenolhydrochlorid bildet bei pH 2 mit Molybdän(VI)-Ionen einen grünen Niederschlag. Dieser kann mit Chloroform extrahiert werden und hat ein Absorptionsmaximum bei 720 mμ. Die Empfindlichkeit der Reaktion beträgt 0,0054 μg Mo pro cm^2 für log I_0/I = 0,001. Die Entwicklung der spektralphotometrischen Mo-Bestimmung schloß eine Untersuchung über p_H-Einflüß, Konzentration des Reagenses, Komplexbildungs- und Extraktionsgrads, Temperaturabhängigkeit und Gültigkeit des Beerschen Gesetzes ein. Die Methode wurde auf die Molybdänbestimmung in Stahl und Gußeisen angewandt.

Résumé—Le chlorhydrate de l'amino-2-chloro-4-benzènethiol fournit un précipité vert avec les ions molybdène(VI) à pH 2. Le précipité peut être extrait au chloroforme et présente une absorption maximum à 720 mμ. La sensibilité de la réaction est de 0,0054 μg de molybdène par cm^2 pour log I_0/I = 0,001. Le développement de la méthode spectrophotométrique de dosage du molybdène comprend une étude sur l'influence du pH, la concentration des réactifs, le taux de formation du complexe et de son extraction, la température et la conformité à la loi de Beer. Cette méthode a été appliquée au dosage du molybdéne dans l'acier et la fonte.

REFERENCES

[1] J. H. Yoe, *J. Chem. Educ.*, 1937, **14**, 170.
[2] H. B. Knowles, *J. Res. Nat. Bur. Stand*, 1932, **9**, 1.
[3] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, Inc., New York, 3rd Ed., 1959.
[4] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Analyt.*, 1944, **16**, 111.
[5] P. Job, *Ann. Chim., France*, 1928, [10] **9**, 113.
[6] W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.
[7] G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis*, J. Wiley and Sons, Inc., New York, p. 58.

Talanta, 1964, Vol. 11, pp. 423 to 431. Pergamon Press, Ltd. Printed in Northern Ireland

PHOTOMETRIC TITRATIONS—VII*

THE CONSECUTIVE TITRATION OF CADMIUM AND ZINC

H. FLASCHKA and F. B. CARLEY
School of Chemistry, Georgia Institute of Technology, Atlanta, Ga., U.S.A.

(*Received* 16 *July* 1963. *Accepted* 31 *July* 1963)

Summary—Zinc and cadmium can be determined in one solution in the following manner. The sample is adjusted to pH 10 with an ammonia-ammonium chloride buffer so that the total ammonia concentration is 0·02–0·03*M*. Murexide is added so that its amount is in at least 5-fold excess over the amount of zinc present. The titration is performed photometrically at about 450 mμ with ethyleneglycol bis(β-amino-ethylether)-*N*,*N*,*N'*,*N'*-tetra-acetic acid (EGTA) as the titrant. The titration curve obtained shows two breaks which are related to the consecutive titration of cadmium and zinc. The influence of calcium impurities in the reagents used has been studied and a method of pretitration is proposed. For this purpose a small amount of zinc is pretitrated and then the sample solution is added. Thus the calcium blank is established for each titration.

IN a previous paper of this series,[1] it was shown that calcium and magnesium can both be determined from a single photometric titration curve. This is achieved by the addition of Calmagite[2] in an amount greater than equivalent to the sum of the two metals, or at least to the magnesium. In that titration, Calmagite does not function in the usual manner as a "step indicator" but, in combination with the magnesium, gives a self-indicating system. Because calcium forms a stronger complex with the titrant (EDTA) than does magnesium, the self-indicating Mg-Calmagite system serves as a "slope indicator" for calcium. Thus a titration curve with two breaks is obtained, the first and second slope changes marking the end-points for calcium and magnesium, respectively.

In the EDTA titration of zinc in ammoniacal solution with Erio T as indicator, the amount of pH 10 buffer added has little influence on the colour change at the end-point. With cadmium, however, increasing amounts of buffer pH 10 cause a decrease in the sharpness of the end-point. Experiments have shown that the addition of large amounts of ammonia pH 10 buffer to a solution containing cadmium and Erio T progressively diminishes the red colour of the cadmium-indicator complex until the pure blue of the free indicator is essentially restored. Under the same conditions, the red colour of the Zn-Erio-T complex is little affected. As expected, Calmagite behaves in exactly the same manner as Erio T but is preferable because it is stable in solution.

From these considerations, it would seem that a Cd-Zn determination analogous to that used for Ca-Mg is feasible. EDTA, however, is not the appropriate titrant in this case because the stabilities of its zinc and cadmium complexes are almost identical. Ethyleneglycol bis(β-amino-ethylether)-*N*,*N*,*N'*,*N'*-tetra-acetic acid (EGTA) is a more favourable titrant because its cadmium complex is stronger than its zinc

---

* Part VI—see ref. 1.

complex, the constants being log $K_{Cd} = 16{\cdot}7$ and log $K_{Zn} = 14{\cdot}5$.[3] Of course, the apparent stability constants must be compared, and these are obtained from a knowledge of the stability constants of the metal-ammonia and metal-dye complexes. At the high ammonia concentrations necessary to decompose the Cd-Calmagite complex, the value of the β_{NH_3}-factor (pH = 10) for zinc is close to 100 times that for cadmium. Because the Zn-Calmagite complex is not decomposed, the Zn-Calmagite β-factor is significant, and thus the logs of the β-factors for cadmium and zinc will differ by more than two units. This indicates that the apparent stabilities of the Cd-EGTA and Zn-EGTA differ by a factor somewhat greater than 10^4, so that a selective titration should be possible. Unfortunately, however, the Zn-EGTA complex is not sufficiently more stable than the Zn-Calmagite complex, so that even a photometric end-point is unsatisfactory. Moreover, galvanometer drift after titrant addition indicated that the reaction $ZnY + CdI \rightarrow ZnI + CdY$ is quite slow. Changing the titration conditions did not improve the situation, so it was necessary to find a more suitable dye.

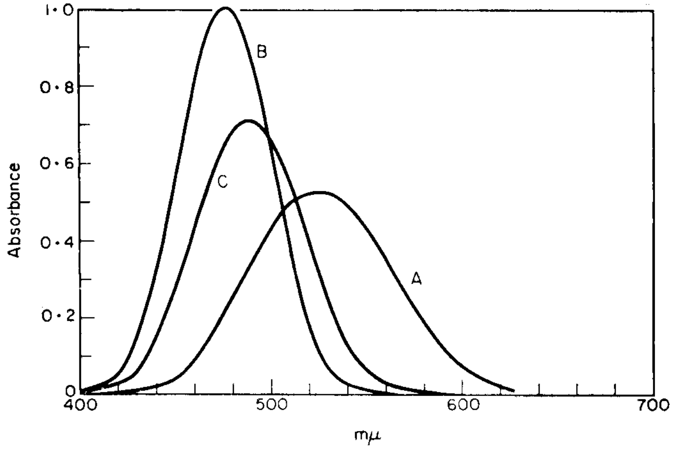


FIG. 1.—Absorbance curves for free Murexide (A), Zn-Murexide (B) and Cd-Murexide (C) at pH 10 (ammonia-ammonium chloride buffer).

Many common metallochromic indicators were investigated and eventually Murexide was found to meet the necessary requirements. Murexide has already been used as indicator in the titration of zinc at pH 8–8·5 in ammonia-free solutions.[4] It was found that the yellow Zn-Murexide complex also persists in solutions buffered to pH 10 with ammonia provided that the ammonia concentration does not exceed certain limits. Also, at some ammonia concentrations where the Zn-Murexide complex is still formed to a considerable degree, the Cd-Murexide complex is largely decomposed. These qualitative findings were substantiated by later quantitative investigations. The spectral curves of free Murexide (A), its zinc (B) and its cadmium (C) complexes at pH 10 are represented in Fig. 1. These curves were obtained with the same total concentration of Murexide and with excess metal ions present to assure complete complex formation. Fig. 2 shows a plot of the difference curve, Zn-Murexide minus Murexide (B-A from Fig. 1), to aid in the selection of an appropriate wavelength. The maximum difference is at 470 mμ and for highest sensitivity this wavelength should be chosen. In practice, however, a somewhat shorter wavelength is more convenient for two reasons. Under the conditions of the titration an excess of Murexide is required, which would provide a considerable background absorbance at 470 mμ. In itself, this is no detriment, although instrument settings are simplified when it is avoided. A second more serious consideration is the instability of the free Murexide in solution. Thus, when considerable amounts of free Murexide are present, and no measures are taken to inhibit its decomposition, a drift of the galvanometer occurs. The decomposition is partly caused by oxidation of the dye, because it is inhibited by deaeration of the solution with nitrogen or by the addition of ascorbic acid. Part of the decomposition is caused by hydrolysis of the dye. At a wavelength of about 450 mμ, the difference is still sufficiently high but the absorptivity of free Murexide is so low that the influence of the decomposition of free Murexide on the optical behaviour of the system is negligible. It may be mentioned in this connection that, as is the case for many other unstable complexing agents, complexed Murexide is stabilised against decomposition. The yellow colour of a solution of Zn-Murexide persists long after the red-violet colour of a solution containing an equal amount of Murexide alone has disappeared.

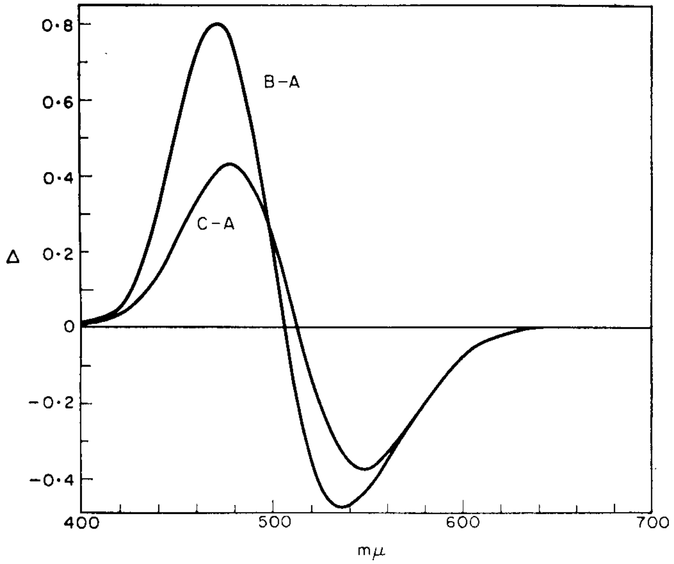


FIG. 2.—Difference curves obtained from Fig. 1.

The difference curve, Cd-Murexide minus Murexide (C-A from Fig. 1), is also shown in Fig. 2. Unless cadmium can be masked completely against the reaction with Murexide, the absorbance of the Cd-Murexide complex must also be considered. (See later.)

The conditions for a working, self-indicating system, zinc-Murexide-EGTA at pH 10, were established as follows. Titrations were performed using $10^{-5}M$ zinc and $10^{-2}M$ EGTA solutions in a 1-cm cell with a 456-mμ interference filter. At first the amount of pH 10 buffer was held constant, and the amount of Murexide was varied. In order to obtain a straight titration curve before the equivalence point, at least a 5-fold Murexide excess over the zinc was necessary; larger excesses did no harm. Next the Murexide concentration was held constant at a sufficient excess and the buffer concentration was varied. Up to approximately 0·01*M* in total ammonia ($[NH_3] + [NH_4^+]$), identical titration curves were obtained. Upon addition of more buffer, the slopes of the titration curves decreased, as was to be expected. A buffer concentration of 0·01*M* is not always sufficient to prevent the precipitation of zinc hydroxide; however, the excess Murexide keeps the metal in solution. This fact makes it necessary to add the Murexide to the titration solution before the sample, when the buffer concentration is low.

Titrations of solutions containing both cadmium and zinc were attempted next.

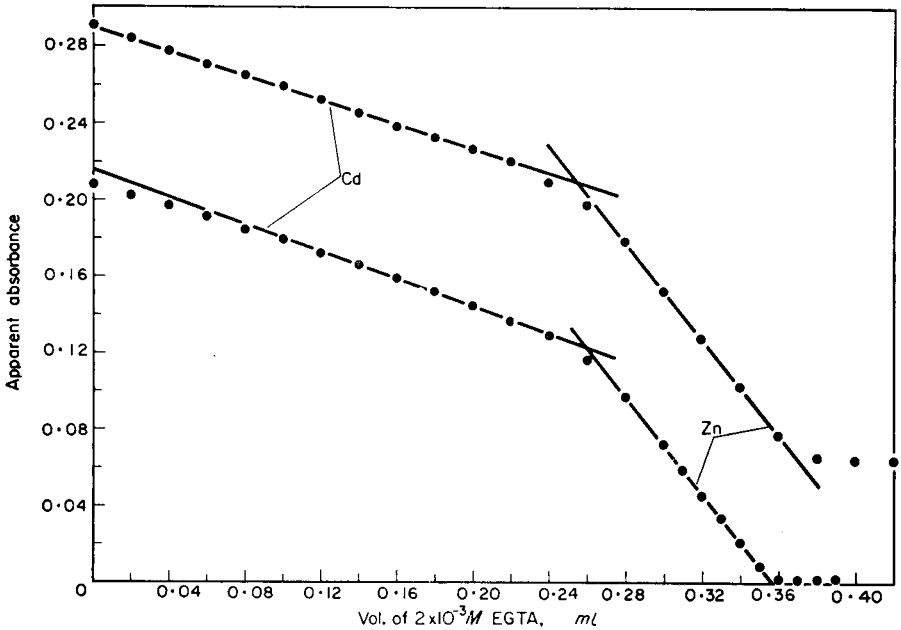


FIG. 3.—Typical curves obtained by titration of a sample containing cadmium and zinc with EGTA.

As expected, cadmium reacts with the titrant before zinc. At low ammonia concentrations (0·01*M* and below), the cadmium segment of the titration curve shows an appreciable slope. With increasing buffer concentration, however, the cadmium segment approaches the horizontal as predicted. The effect of buffer concentration on the zinc segment is less pronounced. Thus a concentration of 0·02–0·03*M* in total ammonia gives the best possible angle at the cadmium end-point without seriously affecting the zinc segment of the curve. The cadmium segment, of course, becomes steeper when the concentration of Murexide is increased. The amount of Murexide necessary is governed only by the amount of zinc present. When the excess of Murexide is not sufficient to complex all the cadmium, the titration curve is nearly horizontal at the beginning and then bends down to the usual cadmium slope. This, however, does not affect the determination because, for the location of the cadmium end-point, only the straight line portion immediately before the abrupt slope change is necessary for the extrapolation.

Typical titration curves with sufficient excess of Murexide showing all three straight portions in nearly perfect fashion are presented in Fig. 3.

It is generally expected that with a very weak complex a curvature should be produced in a titration curve. Thus it is rather unexpected that, with the deliberately weakened Cd-Murexide complex, such a perfect straight line is obtained. Similar reasoning holds as for the analogous conditions of the calcium segment of the Ca-Mg-titration described in a previous paper of this series.[1] The full mathematical treatment of this situation is reserved for another publication, and here only a simplified derivation will be given.

Consider a metal ion, M, reacting with a dye, I, according to

$$M + I \rightleftarrows MI.$$

(Charges are omitted because they are irrelevant to the point in question.) Only MI is assumed to absorb at the wavelength selected. Hence

$$A = \varepsilon b \times [MI].$$

The stability constant of the complex MI is given by

$$K = \frac{[MI]}{[M]\,.\,[I]} \tag{1}$$

The following two equations must hold:

$$C_M = [MI] + [M] \tag{2}$$

$$C_I = [MI] + [I] \tag{3}$$

When the dye is in considerable excess the condition $C_I \gg C_M$ is given and consequently also

$$C_I \gg [MI].$$

Using this and substituting (2) and (3) in the expression for the equilibrium constant (1), one obtains

$$K = \frac{[MI]}{(C_M - [MI])C_I} \tag{4}$$

Solving for [MI] results in

$$[MI] = \frac{KC_I}{KC_I + 1}\,.\,C_M = \text{const.} \times C_M \tag{5}$$

and finally,

$$A = \varepsilon b.\ \text{const.} \times C_M = \text{const.}' \times C_M \tag{6}$$

Thus the absorbance is directly proportional to the total metal ion concentration regardless of how weak the complex may be. If these findings are applied to a titration the following reasoning holds: assume that the metal is titrated with a complexing agent, Y, and that the titration complex, MY, is of so high a stability that its dissociation can be neglected to a first approximation. Then C_M in equation (6) is the concentration of metal ion not complexed by the titrant, and consequently a straight-line titration curve is obtained even with a very weak metal-dye complex.

It is of interest to speculate in this connection as follows. Many photometric determinations (not titrations!) employ rather weak complexes and the procedure requires "addition of a considerable excess of chromogenic agent in order to shift the equilibrium to virtual completion, so that a straight calibration curve is obtained". It is entirely possible that there is no shift to completion at all, but rather that the straight calibration curve is a consequence of the situation discussed above.

Because many other metal ions (of notable interest are lead, copper, nickel and cobalt) also give yellow Murexide complexes, the selectivity of the proposed titration is not expected to be high. Selective masking and demasking may improve the situation but no investigations in this direction were undertaken. Separation of Cd + Zn is possible by several methods (ion exchange, paper chromatography, solvent extraction) so that the method described may be applied after such a separation is effected. Only the influences of magnesium and calcium were investigated, because these two metals, present as impurities in the reagents used, or introduced by dust, may affect the results seriously, especially when small amounts of zinc and cadmium are to be determined.

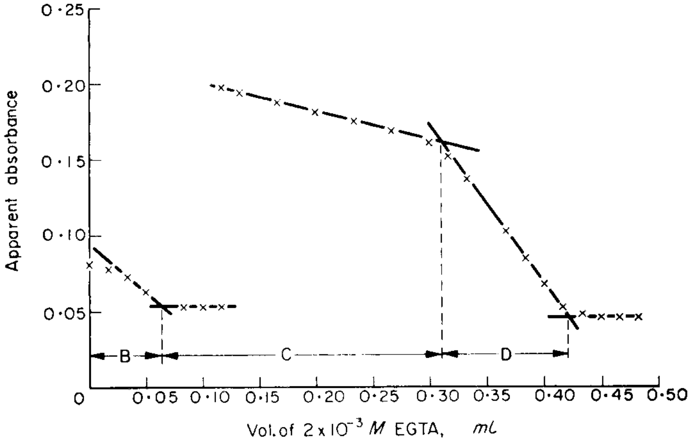


FIG. 4.—Calculation of an analysis of a Cd-Zn mixture using the pretitration method. Let A stand for the EGTA (ml) equivalent to the known amount, P, of zinc added for the pretitration.

Then: pretitrated impurity of Ca $\hat{=}$ B − A ml
Cd $\hat{=}$ C + A ml
Zn $\hat{=}$ D − A ml.

Magnesium was found not to interfere at all, as was to be expected from the low stability constant of its EGTA complex (log K = 5·4) and the fact that it shows only very little tendency to complex with Murexide. Calcium is titrated after cadmium and before zinc. The slope of the calcium segment is virtually identical to that of the cadmium segment so that the sum Cd + Ca is obtained at the "cadmium end-point". Thus cadmium may be corrected for any calcium blank established. Unfortunately the calcium blank is not constant over a long period of time. Water and reagent solutions prepared in the way described in the experimental part are at the beginning virtually free from calcium. But on the repeated opening of the plastic bottles dust enters the solution and the blank becomes noticeable and increases with time. It is, therefore, most convenient to establish the blank for each titration *via* a pretitration. For this purpose the buffer solution containing the Murexide is placed in the titration cell and diluted to the desired volume. Then a small, accurately known amount of zinc is introduced and titrated. After this pretitration the sample solution is introduced and the titration is performed as usual. The amounts of titrant required for the cadmium and zinc in the sample are obtained from the titration curve as shown in Fig. 4. This method, of course, corrects for only those impurities (calcium or any other metals with similar interference mechanisms) present in the reagents, but any calcium in the sample solution is still cotitrated with the cadmium.

Zinc or cadmium alone may also be titrated using the pretitration technique and in this case the amount of zinc added initially need not be accurately known. The amount of metal present in the sample is obtained simply from the difference of two zinc end-points.

The accuracy and precision of the method are satisfactory. Table I shows a selection of results for titrating zinc alone and cadmium alone, as well as zinc and cadmium together, using the pretitration technique.

EXPERIMENTAL

Apparatus

The phototitrator described in Part II of this series was used.[5] An improvement was found to be necessary. At the wavelength selected, strong deviations from Beer's law were observed initially. These were eventually traced to insufficient monochromacy. The filter used not only passed light of the nominal wavelength but showed also a transmittance peak in the near infrared. Hence a heat ray absorbing filter was permanently positioned in the light beam behind the interference filter. Some titrations were initially performed in the micro cell assembly described in Part VI of this series.[1] It was then possible to titrate as little as a few μg of cadmium and zinc. In this case a Beckman Spinco ultra-microburette was employed. Again, however, serious dust problems were encountered under the prevailing conditions. Therefore a macro cell of 35-ml capacity and a light path of 2 cm were used, and the titrant was delivered from a 1-ml micro burette. An interference filter of 456 mμ and in some cases of 444 mμ nominal wavelength has employed.

Reagents

All reagents were of highest purity. The water used was deionised water, redistilled using a condenser tube of polyethylene. All solutions were stored in polyethylene bottles. The buffer solution was prepared by mixing ammonia and hydrochloric acid solutions which had been purified by isothermal distillation. The distillations were accomplished by placing a beaker containing the concentrated commercial reagent along with a polyethylene beaker containing redistilled water in a desiccator (without desiccant) for a day or two. The total concentration of ammonia in the buffer was $2M$.

Stock solutions of zinc and cadmium (about $0{\cdot}1M$) were prepared by dissolving appropriate amounts of highest purity metal in HNO_3 followed by dilution with redistilled water.

Stock solutions of chelons (of about $0{\cdot}1M$) were prepared by dissolution of the reagent in redistilled water (a few pellets of NaOH were added, if necessary, to effect solution).

The stock solutions were standardised by well established complexometric methods.

More dilute solutions were prepared by quantitative dilution of these stock solutions.

Procedure

Place about 25 ml of water in the absorption cell. Add 0·2 ml of buffer and about 0·5–1 mg of Murexide.* Adjust the light to give a galvanometer reading of about 90 S.D. (or 180 S.D. with zero suppressed to −100). Add 0·2–0·5 ml (exactly measured) of a $5 \times 10^{-4}M$ zinc solution and titrate with $2 \times 10^{-3}M$ EGTA until the curve shows 2–3 points of the horizontal after the zinc end-point (see Fig. 4). Add the unknown sample and titrate again.† Plot the results and evaluate the curve as shown in Fig. 4.

---

* It is not necessary to weigh the Murexide accurately. One may dilute Murexide by grinding it with sodium chloride and add a certain amount with a spoon of appropriate size. However, it is much simpler to add Murexide (diluted or undiluted) to the solution containing buffer until a predetermined galvonometer reading is obtained. The amount of Murexide is not at all critical as long as there is a sufficient excess over the zinc.

† For samples with very high metal contents it may be necessary to operate with a "sectioned titration curve". See Part VI in this series for details.[1]

Table I.—Titration of zinc and cadmium with EGTA

Zinc						Cadmium					
4·71 × $10^{-4}M$, *ml*			$10^{-7}g$			5·06 × $10^{-4}M$, *ml*			$10^{-7}g$		
Taken	Found	Diff.	Taken	Found	Diff.	Taken	Found	Diff.	Taken	Found	Diff.
0·474	0·477	+0·003	146	147	+1						
0·480	0·484	+0·004	148	149	+1						
0·514	0·511	−0·003	158	157	−1						
0·578	0·576	−0·002	178	177	−1						
0·627	0·620	−0·007	193	191	−2						
0·742	0·756	+0·014	228	233	+5						
0·881	0·871	−0·010	271	268	−3						
0·910	0·910	±0·000	280	280	±0						
1·121	1·100	−0·021	345	339	−6						
						0·916	0·914	−0·002	521	520	−1
						1·063	1·068	+0·005	605	607	+2
						1·313	1·306	−0·007	747	743	−4
0·353	0·340	−0·013	109	105	−4	0·521	0·530	+0·009	296	301	+5
0·429	0·427	−0·002	132	131	−1	1·526	1·530	+0·004	868	870	+2
0·500	0·492	−0·008	154	151	−3	1·000	0·997	−0·003	569	567	−2
0·500	0·495	−0·005	154	152	−2	1·000	0·983	−0·017	569	559	−10
0·529	0·552	+0·023	163	170	+7	5·005	5·000	−0·005	2846	2844	−2
0·555	0·564	+0·009	171	174	+3	1·036	1·038	+0·002	589	590	+1
0·735	0·716	−0·019	226	220	−6	1·637	1·621	−0·016	931	922	−9
1·915	1·910	−0·005	590	588	−2	0·577	0·569	−0·008	328	324	−4

Acknowledgment—Part of this work was performed under a grant of the National Science Foundation. This aid is gratefully appreciated.

Zusammenfassung—Zink und Cadmium können in einer Lösung wie folgt bestimmt werden. Die Probe wird mit Ammoniak-Ammoniumchlorid-Puffer auf pH 10 gebracht, sodass die totale Ammoniak-Konzentration 0.02–0.03 m beträgt. Sodann wird Murexid in mindestens fünffachem molaren Überschuss (auf Zink bezogen) eingetragen. Es wird photometrisch bei 450 mμ titriert. Die erhaltene Titrationskurve zeigt zwei Knicke, deren erster dem Cadmium- und deren zweiter dem Zink-Endpunkt entspricht. Der Einfluss von Calciumverunreinigungen in den Reagenzien wurde studiert und eine Vortitration wird vorgeschlagen. Hierbei wird erst eine kleine, genau bekannte Menge an Zink vortitriert und dann die Probe zugesetzt. So lässt sich der Cacliunblindwert der Reagenzlösung für jede Titration in Rechnung stellen.

Résumé—Le zinc et le cadmium peuvent être dosés dans une solution unique de la manière suivante. L'échantillon est amené à pH 10 par addition d'une solution tamponnée ammoniaque-chlorure d'ammonium et composée de telle sorte que la concentration totale en ammoniaque soit de 0,02–0,03 M. On ajoute du murexide en quantité telle su'elle représente un excès d'au moins cinq fois sur la quantité de zinc présente. Ce dosage est effectué par photométrie à environ 450 mμ et en présence d'EDTA comme agent titrant. La courbe de dosage obtenue montre deux cassures correspondant aux neutralisations successives du cadmium et du zinc. L'influence des impuretés calciques dans les réactifs utilisés a été étudiée et une méthode de prédosage proposée. Dans ce but, une petite quantité connue de zinc est prédosée et l'on ajoute la solution à analyser. Ainsi le taux de calcium dans l'essai témoin est établi pour chaque dosage.

REFERENCES

[1] H. Flaschka and P. Sawyer, *Talanta*, 1962, **9**, 249.
[2] F. Lindstrom and H. Diehl, *Analyt. Chem.*, 1960, **32**, 1123.
[3] J. H. Holloway and C. N. Reilley, *ibid.*, 1960, **32**, 249.
[4] J. S. Fritz, M. O. Fulda, D. L. Margerum and E. I. Lane, *Analyt. Chim. Acta*, 1954, **10**, 513.
[5] H. Flaschka and P. Sawyer, *Talanta*, 1961, **8**, 521.

Talanta, 1964, Vol. 11, pp. 433 to 439. Pergamon Press Ltd. Printed in Northern Ireland

SELECTIVE DETERMINATION OF TRACE AMOUNTS OF COBALT USING THE SORPTION OF $Co(PHEN)_3^{2+}$ ON SILICA

FRANTIŠEK VYDRA
Polarographic Institute of the Czechoslovak Academy of Science
Analytical Laboratory, Jilská 16, Prague 1
Czechoslovakia

(*Received* 20 *June* 1963. *Accepted* 20 *August* 1963)

Summary—Sorption of $Co(Phen)_3^{2+}$ on silica is not affected by EDTA or citric acid in appropriate conditions of acidity. This fact has been used for the selective determination of microgram amounts of cobalt. Desorption of $Co(Phen)_3^{2+}$ is carried out from an alkaline aqueous-methanolic solution of ammonium formate, and cobalt is determined indirectly, colorimetrically, *via* ferroïn. Special attention has been paid to the determination of trace amounts of cobalt in the presence of iron.

As previously mentioned,[1] the complex of Co^{II} with 1,10-phenanthroline (Phen), [$Co(Phen)_3^{2+}$ (pK = 20·1)], can be sorbed on silica quantitatively over a large pH range even in the presence of EDTA and citric acid. Anionic complexes of metals with EDTA and citric acid are not sorbed on silica, and therefore it is possible to use these reagents to increase the selectivity of the sorption of $Co(Phen)_3^{2+}$, and thus also to permit the determination of cobalt. The formation of ion association complexes [$Co(Phen)_3^{2+}, 2X^-$] which increases at high concentrations of X^- has been similarly used for the desorption of $Co(Phen)_3^{2+}$, sorbed on silica, as well as for the desorption of ferroïn.[2,3] Complexes of this type, where X^- indicates anions of some monobasic acids, *e.g.*, formic, acetic, trichloro- and monochloroacetic, are, to a certain degree soluble in water, and are very soluble in a mixture of methanol and water.

After elution of the $Co(Phen)_3^{2+}$, cobalt is determined in the solution colorimetrically;[4] the cobalt bound in the phenanthroline complex is oxidised with $iron^{III}$, and the concentration of the resulting ferroïn is determined colorimetrically.

This paper describes a number of influences on the sorption of $Co(Phen)_3^{2+}$ on silica, and on its use for the selective determination of trace amounts of cobalt. Special attention has been paid to the determination of cobalt in the presence of $iron^{III}$ which results in the oxidation of $cobalt^{II}$ to $cobalt^{III}$ with an excess of Phen, and the formation of an equivalent amount of ferroïn.

EXPERIMENTAL

Reagents

Silica: Silica of pore size 85 Å and particle size 0·15–0·20 mm, activated at 120° was used (if not stated otherwise) for the sorption, which was carried out on a column of 16 mm internal diameter and 50 mm in height. The "silica pH" was adjusted to the required value by washing with a suitable buffer solution.

1,10-Phenanthroline solution: 0·1*M*: Prepared by dissolving 18 g of reagent-grade 1,10-phenanthroline in hot water, acidifying with 5 drops of acetic acid and diluting to 1 litre.

Cobalt chloride solution: $10^{-4}M$: Prepared by dissolving $CoCO_3$ (Kahlbaum, Ni-free) in a minimum amount of HCl and diluting it with water.

Salt solutions: 1*M* solutions of ammonium formate, acetate, tri- and monochloroacetate were prepared by the solution of the appropriate salts or acids in redistilled water, and adjusting the pH to 9·5 with aqueous ammonia.

EDTA solution: 1*M*: Prepared by dissolving 372 g of reagent-grade EDTA in warm water, making alkaline with aqueous ammonia (1 : 1) and diluting to 1 litre. The pH of the resulting solution should be 8.

Buffer solutions: Prepared by potentiometric neutralisation of suitable acids (trichloro-, monochloroacetic, acetic or boric acid (with aqueous ammonia) to give a final concentration of *ca.* 1*M*.

Other solutions prepared from reagent-grade chemicals, and standardised by recommended procedures.

Apparatus

Optical densities were measured with a Pulfrich photometer (Zeiss, Jena, East Germany) equipped with an arrangement for objective measuring—Elpho II. pH values were measured with a glass electrode and pH meter Multoscop V (Labor. potřeby, Prague, Czechoslovakia).

Sorption of $Co(Phen)_3^{2+}$ *on silica*

In most cases the influence of factors on the sorption of $Co(Phen)_3^{2+}$ on silica was followed by a kinetic method, which was also used for analytical purposes. As already mentioned, the changes in the concentration of the Co^{II} complex with phenanthroline were followed by indirect colorimetric measurements, *via* ferroïn. The reaction used occurs quantitatively even in an aqueous-methanolic medium, under identical conditions. The procedure, except in cases mentioned explicitly, was as follows.

Procedure: To a measured amount of 10^{-4} or $10^{-3}M$ $CoCl_2$ was added a known amount of 1*M* EDTA solution or 1*M* citric acid; alternatively the pH was adjusted by addition of 5 ml of 1*M* buffer solution. To this solution, 1 ml of 0·1*M* phenanthroline was added, and after a further adjustment of the pH, the volume of the solution was adjusted to ~25 ml. The sorption on the silica column was carried out, after adjusting the pH of the silica, at a flow rate of about 2 ml/min. The washing of the column after the sorption was carried out with 25 ml of a 0·1*M* buffer solution with a pH of the same value as during the sorption, and, finally, with 10 ml of water. The desorption of the sorbed $Co(Phen)_3^{2+}$ was carried out with 15 ml of *ca.* 1*M* solution of ammonium formate of pH 9·5, containing, in every 100 ml, 1 ml of 0·1*M* phenanthroline* and 15 ml of methanol. The desorption can be carried out reliably at the same rate as the sorption. The washing of the column was carried out with 10 ml of water. The pH of the solution, containing $Co(Phen)_3^{2+}$, was adjusted with HCl (1 : 1) to ~3. One ml of 0·1*M* phenanthroline was added, and 2 ml of *ca.* $10^{-3}M$ $FeCl_3$ (containing no Fe^{II}). The volume was adjusted to 50 ml, and the extinction of the ferroïn was measured after 15 min, in 2-cm cells at 510 mμ, against a blank at pH 3, containing, in the same volume, the same amount as the sample of $FeCl_3$ and Phen. The evaluation was read from a calibration curve, obtained by adding to 2–15 ml of $10^{-4}M$ $CoCl_2$, 1 ml of 0·1*M* Phen, 1 ml of $10^{-3}M$ $FeCl_3$ and 5 ml of buffer solution of pH *ca.* 3, and diluting to 50 ml as in the case of the sample solution.

RESULTS AND DISCUSSION

Influence of pH, EDTA and citric acid

The influence of pH, EDTA and citric acid was studied on the sorption of 29·5 μg of cobalt. The curves in Fig. 1 show that the sorption of cobalt is complete in the pH range 2–7·5 (curve 1), even in the presence of citric acid (curve 2). In the solution of 0·1*M* EDTA the sorption of $Co(Phen)_3^{2+}$ is not influenced in the pH range 6·5–8·5. At lower pH values, however, EDTA interferes by forming chelates. At higher pH values, the presence of EDTA reduces the hydrolysis of Co^{II} (curve 3). These examples show the dependence of the apparent stability constants of $Co(Phen)_3^{2+}$ and of the Co–EDTA complex on pH.

Influence of rate of sorption, dilution and ionic strength

Under given conditions, the sorption of 29·5 μg of cobalt in 25 ml of solution is quantitative, even at a flow rate of 6 ml/min, which was, in our case, the maximum possible rate.

---

* Phenanthroline must be present in the solution, otherwise there will be a partial hydrolysis of $Co(Phen)_3^{2+}$, and its desorption is then not quantitative.

The influence of the ionic strength was tested by sorption of $Co(Phen)_3^{2+}$ from saturated solutions of some salts of alkali metals (*e.g.*, 29·5 μg of Co were sorbed with an error of —4·2% from a saturated solution of NaCl.

Capacity of silica

It was found by using a kinetic method that a silica column (50 mm high and 16 mm in diameter) at pH 3·5 and a flow rate of 2 ml/min sorbs quantitatively as much as 1·16 mg of Co as $Co(Phen)_3^{2+}$.

Using a static method the capacity of the silica was determined in the following way: 1 g of silica was shaken intensively for 5 hr on a shaking machine with a solution of 5 ml of 5×10^{-2} *M* $CoCl_2$, 5 ml of 1*M* buffer solution of pH 3·5, 10 ml of 10^{-1} *M* Phen, the volume being adjusted to 25 ml. The change of the concentration of $Co(Phen)_3^{2+}$ was determined colorimetrically by measuring the intensity of the yellow coloration of the complex at 410 mμ (pH *ca.* 3.)[5] It was found that at pH *ca.* 3·5 6·35 mg of cobalt is sorbed on 1 g of silica. During the study of the mechanism of the sorption,[6] it was found that the capacity of silica for $Co(Phen)_3^{2+}$ is effectively unaltered in the pH range 1·5–9·5.

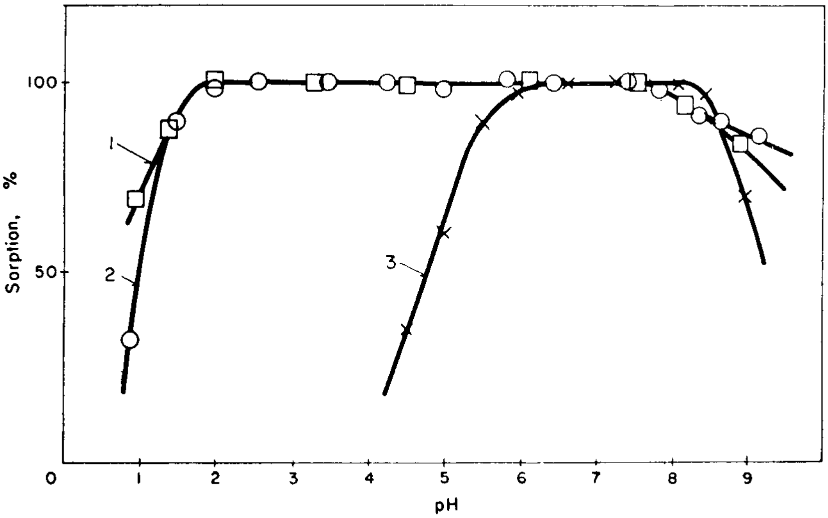


FIG. 1.—Influence of pH on sorption of $Co(Phen)_3^{2+}$ on silica

1—in 0·1*M* buffer solutions.
2—in 0·1*M* citric acid.
3—in 0·1*M* EDTA.

The capacity of silica is influenced by the size of grain and of pores in the same way as in the sorption of ferroïn.[2] These results apply to the commonly used silica (pore size 85 Å, grain size 0·15–0·20 mm). With decreasing grain size of silica the capacity rises abruptly. Because of the resistance of a column of finer silica, the application to sorption under kinetic conditions is rather problematical. For the determination of trace amounts of Co— which is the aim of the work described in this paper—silica with a higher capacity is not necessary. The pore size in a given range does not influence appreciably the sorption of $Co(Phen)_3^{2+}$(32·65 and 85 Å); larger pore silica (150 Å), however, has a very small capacity.

Reagents for desorption

Alkaline solutions (pH 9·5–10) of ammonium salts of some acids may be used in the same way as for the desorption of ferroïn sorbed on silica. Instead of the more usual ammonium formate, it is possible to use, under the same conditions, ammonium salts of trichloroacetic, monochloroacetic and acetic acids. To prevent the hydrolysis of $Co(Phen)_3^{2+}$, the presence of phenanthroline is necessary just as when formic acid is used. The minimum volume necessary for the desorption under the same conditions was obtained when ammonium formate and trichloroacetate were used. Methanol lowers still further the volume of the minimum amount of elution mixture.

Analytical application

It is advantageous for the analytical application that the sorption of $Co(Phen)_3^{2+}$ on silica is quantitative, even from solutions of high ionic strength. Very dilute solutions can be concentrated by sorption from a large volume and desorption by a minimum volume. It is possible to use the masking properties of EDTA and citric acid to increase the selectivity of the determination of cobalt. For a rapid determination of cobalt it is important that the sorption of $Co(Phen)_3^{2+}$ on silica can be carried out reliably at a comparatively high flow rate and that the final colorimetric determination does not need a special treatment of the solution of $Co(Phen)_3^{2+}$, and is rapid.

Also, the fact that the sorption is carried out on an inexpensive type of silica, needing no special treatment, is an advantage in the analytical application. The procedure for the analytical utilisation of the sorption of $Co(Phen)_3^{2+}$ on silica is practically identical with the procedure for the sorption. In the sequel, only results will be given, and any digressions from the given working procedure.

Reliability of determination

With the above procedure, at pH 7, a number of determinations of 29·5 μg–1·16 mg of cobalt were carried out, taking care to maintain the excess of phenanthroline during the sorption at least to ten-fold (molar). In the case of larger concentrations of cobalt, the solution containing $Co(Phen)_3^{2+}$ was adjusted to a volume suitable for a sensitive determination of cobalt *via* ferroïn. The results obtained show that, in the given concentration range, cobalt is determined with an average relative error of ±3·7%.

Selectivity of determination

The influence of interfering ions on the formation and sorption of $Co(Phen)_3^{2+}$ ($pK = 20{\cdot}1$) on silica is identical to that in the case of $Fe(Phen)_3^{2+}$ ($pK = 21$). The formation of complexes of cobalt[11] is affected especially by those ions which also form with Phen stable soluble complexes or less soluble ion associates (*e.g.*, Ni, Cu, Zn, Cd, Hg, Ag, W, Mo). The course of the sorption on silica is also affected by other metal ions which hydrolyse at optimal conditions, forming hydroxo complexes (which are also sorbed on silica), giving in water partly soluble hydroxides which inhibit the smooth course of the reaction (*e.g.*, Bi, Ti, Cr, Al, Sn, Sb, *etc.*)

To avoid the separation of cobalt from these interfering ions, their influence can be prevented, in most cases, by utilising the complex-forming properties of EDTA and citric acid, complexes of these reagents not being sorbed on silica, because of their anionic character.

Masking with EDTA

In the pH range 6·5–8·5 it is possible, with EDTA, to mask those metals which, under given conditions with this reagent, form complexes which are stable enough to prevent a reaction with phenanthroline or a hydrolysis.

Working procedure: To a solution of 29·5 μg Co and of the interfering metal, an amount of 1*M* solution of EDTA is added, sufficient to bind the metal quantitatively. The pH of the solution is adjusted to *ca.* 7, the volume to *ca.* 25 ml, and 1 ml of 0·1*M* Phen is added. The sorption of $Co(Phen)_3^{2+}$ and its determination is carried out according to the procedure used during the sorption. Metals which hydrolyse easily and do not form very stable complexes with Phen can be masked with EDTA to allow the determination of trace amounts of cobalt in their presence.

In this way 29·5 μg of cobalt were determined in the presence of *ca.* 100 mg of Pb, Mn, Be, Zr, Sc, In, La, Al, Cr or Bi with an error not exceeding ±4% rel. It is probable that the determination of cobalt is possible in the presence of an even larger excess of these metals. In the case of Al and Cr it is necessary to boil the solution after adding EDTA—both ions react slowly with EDTA at normal temperature. During the sorption of $Co(Phen)_3^{2+}$ in the presence of higher concentrations of Cr bound with EDTA, a sorption of hydroxo complexes of chromium occurs (a violet layer on the column); these are not desorbed in alkaline medium by formate, and do not influence the determination. The elution can be carried out with dilute acid.

Only limited concentrations of metals which form stable complexes with Phen and which have stability constants nearly equal to, or higher than, the complexes of EDTA (Cu, Ni, Cd, Zn, Fe) can be screened. In this way 29·5 μg of Co were determined with an error not exceeding ±5% rel., in the presence of 23·6 mg of Ni, 15·5 mg of Cu, 225 mg of Cd and 130 mg of Zn. In the case of Cd and Zn it is necessary to boil and cool the solution after adjustment of pH and addition of Phen, otherwise the Co^{II} complex forms, and the results are low.

Masking with citric acid

Citric acid does not affect the sorption of $Co(Phen)_3^{2+}$ on silica, even at high concentrations. For a number of metals, pH 3·5–4 is optimal, as in the masking of metals which affect the formation and sorption of ferroïn. Most multivalent metals, *e.g.*, Sn, Sb, Bi, Tl and Zr, can be screened by citric acid when hydrolysis is to be prevented; the same applies to metals which form with Phen practically insoluble associates (W, Mo). An excess of sodium citrate must be used in most cases to prevent hydrolysis, and therefore the formation of complexes with Phen.

Procedure: For example for the determination of 29·5 μg of cobalt in the presence of 47 mg of Mo (as molybdate). About 10 ml of 1*M* sodium citrate are added to the solution, the pH is adjusted to 3·5–4, and 1 ml of 0·1*M* Phen is added. The sorption, desorption and determination of cobalt *via* ferroïn is carried out in the same way as before.

With the method described, the same amount of cobalt was determined even in the presence of 75 mg of W and 82 mg of Bi. The relative error of the determination did not exceed ±3·5%.

Determination of cobalt in the presence of iron

Special attention was paid to this case because Fe^{III} and Fe^{II} form with Phen very stable complexes, and because of the redox reaction[8] which occurs over a large pH range in the presence of cobalt, bound as $Co(Phen)_3^{2+}$:

$$Fe_2(OH)_2(Phen)_4^{4+} + 2Co(Phen)_3^{2+} + 2HPhen^+ \rightleftharpoons 2\,Fe(Phen)_3^{2+} + 2Co(Phen)_3^{3+} + 2H_2O \quad (2)$$

which is the reaction used for the final indirect colorimetric determination of cobalt.

For the determination with milligram amounts of Fe^{III}, the amount of ferroïn formed corresponds to the concentration of cobalt, which permits the determination of this metal[4]. Reaction (2) can be applied even for the concentration or separation of ferroïn from a mixture.

With a molar ratio Fe:Phen = 1:1, reaction (2) proceeds quantitatively, but all the excess of Fe^{III} bound as $Fe_2(OH)_2(Phen)_4^{4+}$ (which is of cationic nature) is sorbed along with ferroïn, and is desorbed by ammonium formate. This phenomenon causes a positive error in the determination, because the yellow-orange coloration of the $Fe_2(OH)_2(Phen)_4^{4+}$ complex is measured together with the coloration of ferroïn. The formation of $Fe_2(OH)_2(Phen)_4^{4+}$ can be considerably reduced by the presence of EDTA, according to the following equation:

$$Fe_2(OH)_2(Phen)_4^{4+} + 2H_2Y^- + 2H^+ \rightleftharpoons 2FeY^- + 2H_2O + 2OH^- + 4HPhen^+, \quad (3)$$

which is strongly influenced by the pH. At higher pH values weaker complexes of Fe^{III}-EDTA than FeY^- can be formed (*e.g.*, $FeOHY^{2-}$), shifting the equilibrium to the left and raising the concentration of the hydro complex Fe^{III}-Phen in equivalent conditions.

When the absolute concentration of Fe^{III} is small, and the excess of EDTA is large, the formation and sorption of $Co(Phen)_3^{2+}$ occurs in the solution at pH 6·5–8·5 in the presence of Phen, and the course of the determination of cobalt does not differ from that already described. At concentrations higher than a few mg of Fe^{III}, the redox reaction (2) occurs even in the presence of EDTA, because the absolute equilibrium concentration of the complex $Fe_2(OH)_2(Phen)_4^{4+}$ is sufficient. It is, however, necessary to carry out the sorption at pH 4–5, and at higher concentrations of iron a blank sorption experiment must be made.

Working procedure: (*a*) To a solution containing 5–100 μg of cobalt and a maximum of 25 mg of Fe sufficient EDTA is added to complex all iron, and then 50% excess. The pH of the solution is adjusted to 4·5, and 1 ml of 0·1*M* Phen is added. After 15 min, the sorption of ferroïn, after the oxidation of cobalt, is carried out, and the ferroïn is desorbed in the same way as described for the sorption of $Co(Phen)_3^{2+}$. The extinction of the ferroïn is measured against water, and the result is evaluated against a calibration curve in the same way as described above. The error in the determination of 29·5 μg of Co in the presence of 25 mg of Fe^{II} does not exceed ±5% rel.

(*b*) In the presence of more than 26 mg of iron a blank has to be carried out with a solution of the same concentration as the sample, in order to eliminate the influence of the coloration of $Fe_2(OH)_2(Phen)_4^{4+}$ which is sorbed and desorbed as ferroïn. The procedure is analogous to that with the sample. After elution the pH is adjusted to the same value, and the resulting solution serves as a comparison in the colorimetry of ferroïn. It is also possible to measure the absorption (at 510 mμ) against water, and subtract the resulting value from the value of the extinction of the sample at the same wavelength. This procedure is suitable for routine determinations of cobalt with similar amounts of Fe (one blank is sufficient). It may be presumed that the above principle and procedure can be used for the determination of small amounts of cobalt in special steels.

Zusammenfassung—Es wurde die Sorption von $Co(phen)_3^{2+}$ an Silicagel studiert, welche bei geeigneten Aciditätsbedingungen weder durch EDTA noch durch Zitronensäure gestört wird, was zur selektiven Bestimmung von μg-Mengen Co ausgenützt wurde. Die Desorption des $Co(phen)_3^{2+}$ wurde mit einer alkalischen, wässrig-methanolischen Ammoniumformiatlösung durchgeführt. Die eigentliche Kobaltbestimmung erfolgte kolorimetrisch auf indirektem Wege über Ferroin. Besondere Aufmerksamkeit wurde der Bestimmung von Spuren Co neben Fe gewidmet.

Résumé—La sorption de $Co(Phen)_3^{2+}$ sur silice n'est pas perturbée par l'addition d'EDTA ou d'acide citrique dans des conditions d'acidité convenables. Ce fait a été utilisé pour le dosage sélectif de quantités de cobalt de l'ordre du μg. La désorption de $Co(Phen)_3^{2+}$ s'effectue au moyen d'une solution alcaline composée de formiate d'ammonum en solution dans le méthanol aqueux, et le cobalt dosé indirectement, par colorimétrie, par l'intermédiaire de la ferroïne. Considérations spéciales sur le dosage des traces de Co en présence de Fe.

REFERENCES

[1] F. Vydra and V. Marková, *Talanta*, 1962, **9**, 449.
[2] *Idem, ibid.*, 1963, **10**, 339.
[3] *Idem, ibid.*, 1963, **10**, 711.
[4] F. Vydra and R. Přibil, *Coll. Czech. Chem. Comm.*, 1961, **26**, 3081.
[5] K. Tachibana, *Mem. Fac. Sci., Kyushu Univ. Ser. C.*, 1961, **4**, 229.
[6] F. Vydra and V. Marková, *J. Inorg. Nuclear Chem.*, in press.
[7] J. A. Hibbits, W. F. Davis and M. R. Menke, *Talanta*, 1961, **8**, 163.
[8] F. Vydra and R. Přibil, *ibid.*, 1959, **3**, 103.

Talanta, 1964, Vol. 11, pp. 441 to 449. Pergamon Press Ltd. Printed in Northern Ireland

ZUR ENTMISCHUNG DER LÖSUNGSMITTEL BEI DER CHROMATOGRAPHISCHEN TRENNUNG—I

SELEKTIVE SORPTION DES FLIESSMITTELS AUF CELLULOSE UND ENTSTEHUNG DER 2. FRONT IN DER PAPIERCHROMATOGRAPHIE

JAN MICHAL und GERHARD ACKERMANN
Institut für Erzforschung Praha, ČSSR und Institut für anorganische und analytische Chemie der Bergakademie Freiberg (Sachsen), DDR

(*Eingegangen am* 17. *Juli* 1963. *Angenommen am* 18. *September* 1963)

Zusammenfassung—Es wird der Verlauf der Entmischung der Lösungsmittel als Wirkung des Trägers (Cellulose, Silicagel) untersucht. Durch Studium der Verhältnisse bei Gemischen von Alkohol, Wasser und Säure konnte bewiesen werden, daß es bei der Verteilungschromatographie zur Entmischung des Fließmittels kommt und daß der Verlauf dieser Entmischung von der Konzentration der Komponenten im ursprünglichen Gemisch abhängt. Es wird die Hypothese ausgesprochen, daß sich an der Grenze zwischen Träger und Lösungsmittelsystem eine Zwischenschicht bildet, an deren Aufbau alle Komponenten des Lösungsmittelsystems beteiligt sind.

NACH der heute allgemein anerkannten Hypothese von Hanes und Isherwood[1] beruht der Trennvorgang bei der Papierchromatographie in erster Linie auf der Einstellung eines Verteilungsgleichgewichts zwischen einem Cellulose-Wasser-Komplex als stationäre Phase und dem Fließmittel als mobile Phase. Dabei ist allerdings zu berücksichtigen, daß die Zusammensetzung des Lösungsmittelgemischs während des Trennvorganges nicht konstant bleibt.

Horner, Emrich und Kirschner[2] verfolgten die Veränderung der Fließmittelzusammensetzung durch das Papier auf die Weise, daß sie in einem geschlossenen Raum ein Lösungsmittelgemisch über das Papier laufen liessen und die abtropfende Flüssigkeit dann refraktometrisch untersuchten. Sie bewiesen dabei, daß beim Durchfluß eine Entmischung des Lösungsmittelsystems eintritt, welche durch die Bindung von Wasser an die Cellulose hervorgerufen wird. Andererseits fanden sie aber bei Gemischen von Phenol mit Wasser eine bevorzugte Sorption der organischen Komponente durch die Cellulose. Sie schlossen daraus, daß die Verhältnisse beim Aufbau der stationären Phase nicht so einfach sind und sprachen die Vermutung aus, daß ein ternärer Komplex aus Cellulose, Wasser und organischem Lösungsmittel entsteht.

Martin[3] benutzte in seiner Arbeit die von Krulla[4] vorgeschlagene Methode und kam damit zum Schluß, daß das Papier Wasser aus dem Lösungsmittelgemisch bis zur Bildung eines bestimmten Gleichgewichtes adsorbiert und daß dabei die Cellulosefasern stark aufquellen.

Da einerseits die bisher erschienenen Arbeiten der einzelnen Autoren recht wenig sichere Ergebnisse enthalten, andererseits aber die Ursache für die Veränderung der Zusammensetzung des Fließmittels für den Trennvorgang und seine theoretische Behandlung von großer Bedeutung ist, erschien uns eine weitere Bearbeitung dieses

Fragenkomplexes wünschenswert. Dabei war zu erwarten, daß mit Hilfe der erhaltenen Ergebnisse auch gleichzeitig die Entstehung der 2. Front bei der papierchromatographischen Trennung aufgeklärt werden kann.

WAHL DER UNTERSUCHUNGSMETHODE

Für die Versuche benutzten wir zunächst die von Martin[3] beschriebene Methode. Sie besteht darin, daß das Fließmittel an einem bei 110°C getrockneten Papierstreifen im geschlossenen, lösungsmitteldampf-gesättigten Raum in üblicher Weise aufsteigt. Nachdem die Flüssigkeitsfront eine bestimmte Höhe erreicht hat, wird der Versuch abgebrochen und das Chromatogramm schnell in vorher markierte Streifen von 2 × 5 cm zerschnitten. Diese werden sofort in getrocknete, austarierte Wägegläser gegeben und gewogen. Durch Subtraktion der Masse des bei 110°C getrockneten Papierstreifens bestimmt man die Flüssigkeitsmenge auf dem Papier in den einzelnen Chromatogrammteilen. Durch Auswaschen mit Wasser und Titration mit 0,05 N Natriumhydroxidlösung beim Studium des Gemisches Alkohol-Wasser-Säure und durch Extraktion mit Alkohol und anschließende Titration mit Karl-Fischer-Reagens beim Studium des Gemisches Alkohol-Wasser wurden die Konzentrationsänderungen im Verhältnis zur Menge des Gemisches in den einzelnen Streifen untersucht.

Abb. 1 zeigt typische Kurven, welche wir dadurch erhielten, daß wir die Masse des Fließmittels (Äthanol 3M an Salzsäure) und die Konzentration der Säure im Verhältnis zu den Rf-Werten des Lösungsmittels verfolgten.

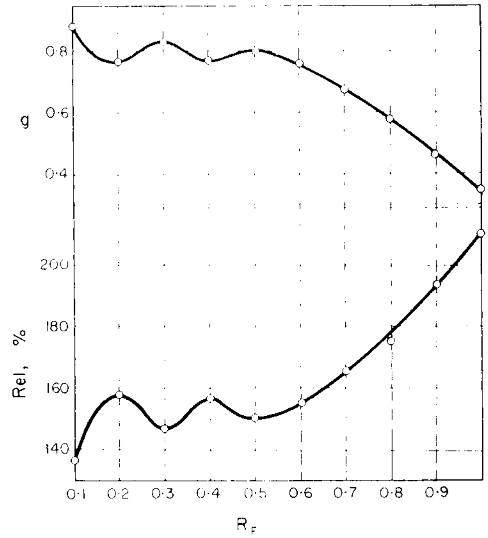


Abb. 1.—Masseänderung des Lösungsmittels (in g) und Änderung der Chlorwasserstoffsäurekonzentration (bezogen auf den Säuregehalt der Ausgangslösung)

Aus den Kurven geht hervor, daß mit der absoluten Masse-Abnahme des Lösungsmittels auf dem Papier der Gehalt an Salzsäure zunimmt. Da sich jedoch diese Abhängigkeit nicht nur im Gesamtbild der Kurve zeigt, sondern auch an den Stellen, an denen es bei der Durchführung der Versuche zu Unregelmäßigkeiten gekommen war, entstand der Verdacht, daß während der Bearbeitung der einzelnen Chromatogrammteile eine selektive Verdampfung auftritt. Es liegt nahe, daß dieser Effekt dann die Form der Kurven maßgeblich bestimmt. Das bedeutet aber, daß das Studium der Entmischung der Fließmittel mit Hilfe des gewählten Untersuchungsverfahrens zu fehlerhaften Ergebnissen führen muß.

Um diese Vermutung zu stützen, haben wir das angewandte Arbeitsverfahren noch etwas näher überprüft.

Für die folgenden Versuche benutzten wir als Fließmittel Methanol, Äthanol, Isopropanol und Butanol mit einem Wassergehalt von 5 Mol/l bei einem Chlorwasserstoff-Gehalt von 3 Mol/l.

Papierstreifen (Whatman Nr. 1, 2 × 7 cm), auf welchen mit Bleistift bei 1 und 6 cm Marken angebracht waren, tauchten wir mit dem unteren Ende in das zu untersuchende Fließmittel und ließen die Front genau bis zur oberen Marke aufsteigen. Danach haben wir die Papierstreifen aus dem Entwicklungsgefäß genommen, den Teil zwischen 1 und 6 cm schnell abgeschnitten und in ein vorher tariertes Wägeglas gebracht, gewogen und anschließend den Gehalt an Wasser bzw. Säure durch Titration bestimmt.

Diesen Vorgang wiederholten wir mit dem Unterschied, daß wir nach Entnahme des Papiers aus der Entwicklungskammer die Streifen 1, 2, 3, 4 und 5 min an der Luft hängen ließen und sie erst dann wie beschrieben behandelten.

Als Beispiel für weitere völlig gleichartig ausgefallene Versuche zeigt Abb. 2 das Verhalten des Gemisches Butanol-Wasser.

Aus Abb. 2a erkennt man, daß erwartungsgemäß mit steigender Lagerzeit an der Luft eine beträchtliche Gewichtsabnahme festgestellt werden kann. Bezieht man, wie Abb. 2b zeigt, die bei der Titration gefundene Wassermenge auf die nach Abb. 2a vorhandene Gesamtflüssigkeit, so ist gegenüber der Ausgangslösung eine erhebliche Zunahme des Wassergehaltes festzustellen, d. h. aber, daß aus dem Fließmittel während der Verarbeitung selektiv der Alkohol verdampft.

Aus diesen Versuchen geht eindeutig hervor, daß mit Hilfe der von Martin[3] beschriebenen Methode keine exakten Aussagen über die Veränderung der Fließmittelzusammensetzung auf dem Papier gemacht werden können.

Wir haben uns deshalb für die Methode der Säulen-Chromatographie entschieden, in welcher wir das zu untersuchende Flüssigkeitssystem über eine Säule aus Cellulosepulver fließen ließen. Es mußte zuvor noch geklärt werden, ob die Verhältnisse auf der Säule mit denen auf dem Papierblatt verglichen werden können.

Zu diesem Zweck untersuchten wir die Trennung von Nickel, Kobalt und Kupfer mit einem Gemisch Aceton-Wasser-Salzäure (8,7 + 0,5 + 0,8) sowohl auf Whatman-Papier wie auch auf der Cellulosesäule. In beiden Fällen arbeiteten wir nach der aufsteigenden Methode. Das Austauscherrohr wurde dazu der Länge nach in 2 Teile zerschnitten und mittels Klebestreifen zusammengehalten.[5] Nach Beendigung der Entwicklung und Öffnen der Säule wurden beide Chromatogramme mit 5%iger Natriumsulfidlösung behandelt. Wie Abb. 3 zeigt, wirken tatsächlich beide Verfahren ähnlich, so daß wir für die weiteren Versuche ohne Bedenken zur Prüfung der Entmischung von Fließmittelsystemen Cellulosesäulen verwenden konnten.

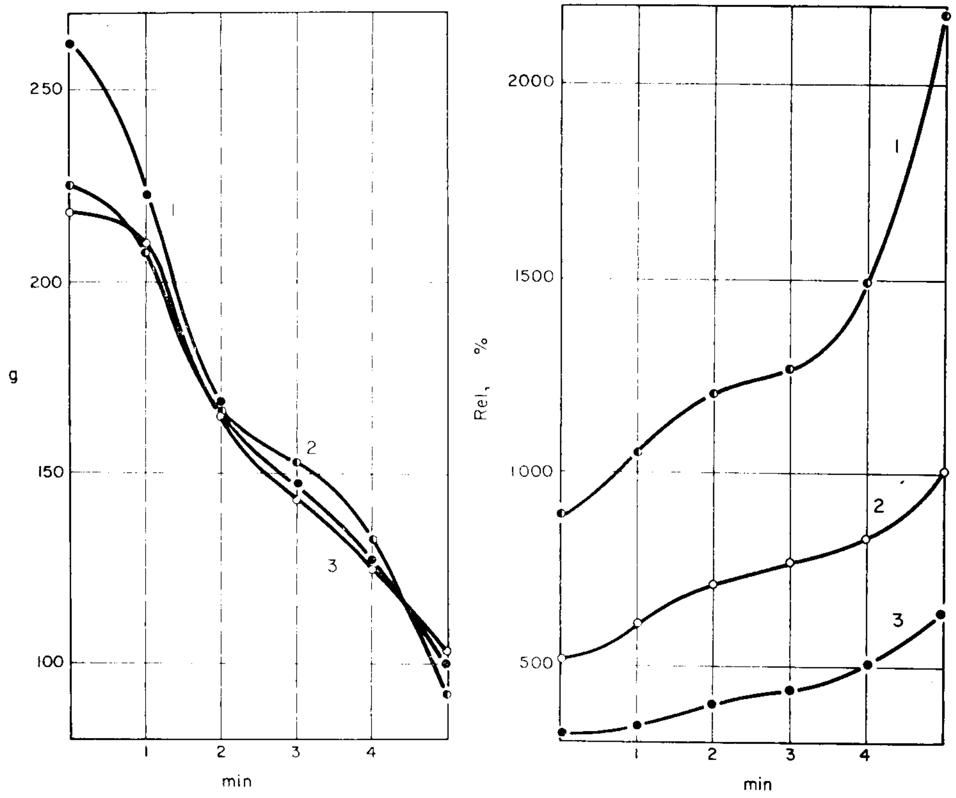
ENTMISCHUNG DER FLIESSMITTEL AN DER CELLULOSESÄULE

Zum Studium des Entmischungsvorganges verwendeten wir Gemische aus Alkohol, Wasser und Chlorwasserstoffsäure. An Alkoholen setzten wir Methanol, Äthanol, n-Propanol, n-Butanol und Benzylalkohol ein.

Durchführung

Über eine an der Luft getrocknete Cellulosesäule (Durchmesser 2,5 cm, Höhe 40 cm, 35 g Cellulosepulver Whatman Standard Grade) floß die zu untersuchende Mischung mit einer Geschwindigkeit von 2 ml pro Minute. Das Eluat wurde in Meßzylindern aufgefangen, aus welchen wir Portionen von 2 ml entnahmen und nach Verdünnung mit dest. Wasser mit 0,05 N Natronlauge gegen Methylrot titrierten.

Alle Alkohol-Säure-Gemische stellten wir so her, daß, 2 ml konz. Salzsäure in einem 100 ml Meßkolben mit reinem, mehrfach destilliertem Alkohol bis zur Marke aufgefüllt wurden.



(a) (b)

ABB. 2.—Veränderung der Zusammensetzung des Fließmittels durch Verdampfen der Alkoholkomponente.

(1) Butanol mit 8% Wasser
(2) Butanol mit 4% Wasser
(3) Butanol mit 2% Wasser

(a): Abnahme der absoluten Lösungsmittelmasse (g Wasser/Mol Cellulose) mit der Zeit
(b): Zunahme des Wassergehaltes mit der Zeit

Abb. 4 zeigt die bei der Untersuchung verschiedener Alkohol-Säure-Gemische erhaltenen Meßergebnisse.

Aus dem Diagramm geht hervor, daß in allen Fällen das Filtrat zu Anfang des Versuches einen wesentlich geringeren Säuregehalt aufweist als die Ausgangslösung. Außerdem kann man erkennen, daß die Menge der von der Säule zurückgehaltenen Salzsäure von der Art des Alkohols bestimmt wird und mit dessen Molekulargewicht wächst. Die Veränderung in der Zusammensetzung des Fließmittels wird

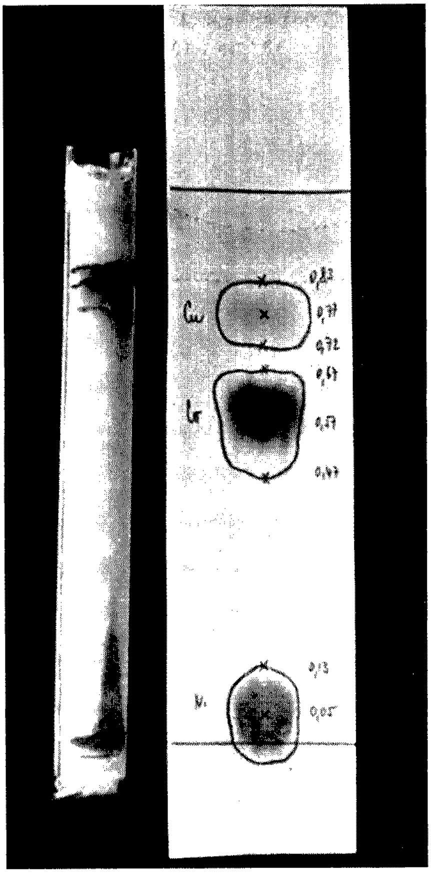


ABB. 3.—Trennung von Nickel, Kobalt und Kupfer mit Aceton-Wasser-Salzsäure. Säulenchromatogramm und Papierchromatogramm

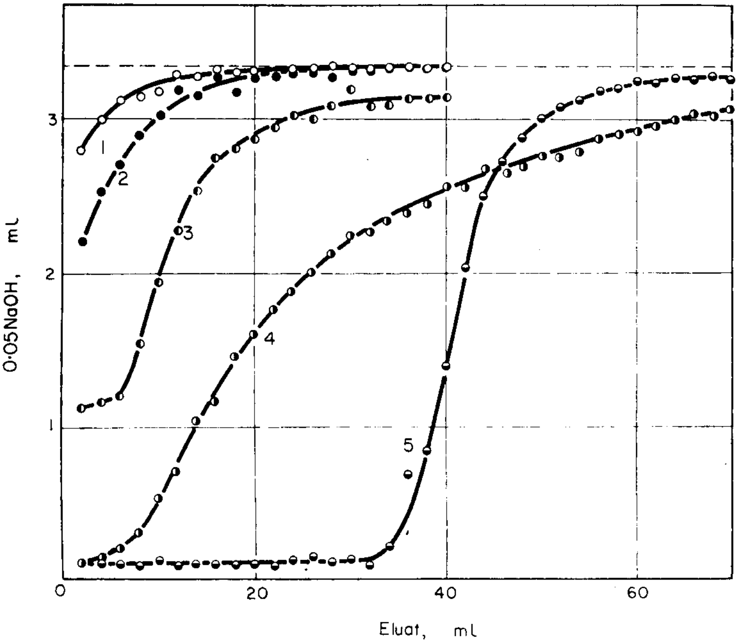


Abb. 4.—Konzentrationsänderung der Chlorwasserstoffsäure im Filtrat.
Cellulosesäule, lufttrocken
(1) Methanol-Salzsäure
(2) Äthanol-Salzsäure
(3) n-Propanol-Salzsäure
(4) n-Butanol-Salzsäure
(5) Benzylalkohol-Salzsäure

augenscheinlich dadurch hervorgerufen, daß die Cellulose selektiv Komponenten des Gemisches bindet und erst nach Sättigung das Lösungsmittel die Säule in seiner ursprünglichen Zusammensetzung durchläuft.

Um zu prüfen, ob die beobachteten Effekte auf den unterschiedlichen Wassergehalt der verwendeten Alkohole zurückzuführen sind, bestimmten wir diesen.

Durchführung

3 ml des verwendeten Alkohols werden mit Karl-Fischer-Lösung nach der Dead-stop-Methode titriert. Das Reagens bereiteten wir auf folgendem Wege. 252 g sublimiertes Jod werden in 400 ml reinem Pyridin gelöst und so lange Schwefeldioxid eingeleitet, bis die Gewichtszunahme 131 g beträgt. Nach Abkühlung wird mit reinstem Methanol auf 2000 ml aufgefüllt. Man läßt 24 Stunden stehen und bestimmt dann den Wirkungswert der Lösung durch Titration einer bekannten Wassermenge. Die Bestimmung erfolgte unter Luftabachluß.

Bei den benutzten Alkoholen fanden wir die folgenden Wassergehalte:

Methanol	4,80%
Äthanol	8,02%
n-Propanol	8,64%
n-Butanol	4,20%
Benzylalkohol	4,03%

Wie man erkennt, ist der Wassergehalt der Alkohole etwas unterschiedlich. Aus dem Vergleich des Verhaltens von Methanol, n-Butanol und Benzylalkohol, die annähernd den gleichen Prozentsatz Wasser enthalten, muß man schließen, daß die

Form der Kurven in Abb. 4 in erster Linie durch die Art des Alkohols bestimmt wird. Äthanol und n-Propanol lassen sich zwanglos in das Bild einorden, obwohl sie etwas mehr Wasser enthalten.*

Unter ähnlichen Bedingungen untersuchten wir auch die Mischung von Aceton bzw. Methyläthylketon mit Salzsäure (2 ml konz. Salzäure mit Keton auf 100 ml aufgefüllt).

Abb. 5 zeigt, daß es auch bei diesen Systemen zu einer Entmischung kommt und daß der Effekt sogar noch deutlicher als bei den Alkoholen auftritt.

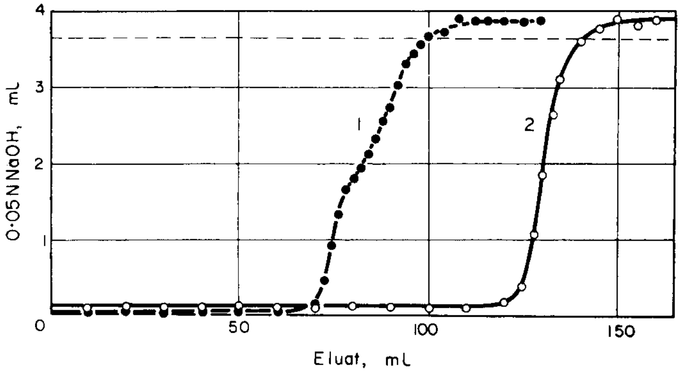


ABB. 5.—Konzentrationsänderung der Chlorwasserstoffsäure im Filtrat. Cellulosesäule, lufttrocken
(1) Aceton-Salzsäure (2) Methyläthylketon-Salzsäure

Um zu klären, ob die Entmischung der Lösungsmittel nur durch Cellulose hervorgerufen wird, prüften wir Gemische von Benzylalkohol mit Chlorwasserstoffsäure und Aceton mit Chlorwasserstoffsäure auch auf einer Silicagelsäule.

Durchführung

Über eine Säule (Durchmesser 2,5 cm, Höhe 40 cm) mit 55 g getrocknetem Silicagel (Korngröße 0,3 bis 0,6 mm) floß die zu untersuchende Mischung mit einer Geschwindigkeit von 2 ml/min. Das Filtrat wurde in gleicher Weise wie bei den vorangegangenen Versuchen geprüft.

Die Kurven der Abb. 6 zeigen, daß die Entmischung des Fließmittels an der Silicagelsäule mit dem Verhalten an Cellulose vergleichbar ist.

Die Befunde beweisen, daß in der Verteilungschromatographie die Entmischung des Lösungsmittels durch den Träger hervorgerufen wird. Die bei den Alkoholen und Ketonen festgestellte Abhängigkeit deutet darauf hin, daß der Zustand an der Grenze zwischen fester und flüssiger Phase nicht so einfach ist wie es im allgemeinen bisher angenommen wurde. Besser charakterisiert werden die Verhältnisse wahrscheinlich durch die Vermutung welche von Horner und Mitarbeitern[2] ausgesprochen worden ist, daß sich nämlich an der Cellulose ein ternärer Komplex Cellulose-Wasser-organisches Lösungsmittel ausbildet.

Die angeführten Versuchsergebnisse sprechen für diese Erklärung, wenn sie auch diese Hypothese noch nicht exakt beweisen. Nehmen wir die Bindung aller Komponenten des Lösungsmittelsystems an der Oberfläche der festen Phase an, so können wir die Verschiebung der Konzentrationskurven bei einer Reihe von Alkoholen und

---

* Über die genauerer Wirkung des Wassergehaltes bei den einzelnen Alkoholen wird später berichtet.

Ketonen durch Änderung des Mengenverhältnisses der Komponenten an der festen Phase erklären.

Über weitere Untersuchungen zu diesem Fragenkomplex soll später berichtet werden.

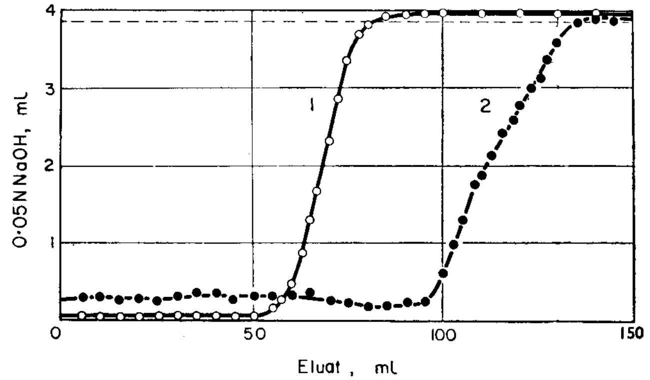


Abb. 6.—Konzentrationsänderung der Salzsäure im Filtrat. Silicagelsäule, getrocknet
(1) Benzylalkohol-Salzsäure (2) Acteon-Salzsäure

ENTSTEHUNG DER ZWEITEN FRONT BEI DER PAPIERCHROMATOGRAPHISCHEN TRENNUNG

Bei den Gemischen von Benzylalkohol mit Chlorwasserstoffsäure und noch deutlicher bei Methyläthylketon-Chlorwasserstoffsäure ist die Abnahme der Säurekonzentration in den ersten Teilen des Filtrates so bedeutend, daß dieser Teil praktisch säurefrei ist. Erst in einiger Entfernung nach dieser praktisch neutral reagierenden Front folgt dann die Säurefront.

Die Bildung zweier Fronten in der Papierchromatographie wird häufig beobachtet. Da sie mit der Entmischung des Fließmittels in unmittelbarer Beziehung stehen muß, widmeten wir auch dieser Erscheinung unsere Aufmerksamkeit. Weil eine selektive Verdampfung des Lösungsmittels hier keine wesentliche Rolle spielen kann, haben wir uns entschlossen, zum Studium der zweiten Front wieder die Methode der Papierchromatographie zu benutzen.

Durchführung

Chromatographiert wurde nach der aufsteigenden Methode auf Streifen von Whatman Papier Nr. 1 (2 × 30 cm). Die Chromatogramme besprühten wir sofort nach Entnahme aus der Entwicklungskammer mit einer 0,05% igen Thymolblaulösung. Der saure Teil des Chromatogramms bis zur zweiten Front erschien dabei rot gefärbt, die Zone darüber gelb.

Um zu zeigen, daß der Einfluß der selektiven Verdampfung bei diesen Versuchen tatsächlich vernachlässigt werden kann, haben wir die Lage der zweiten Front auf der Cellulosesäule (Abb. 4, Kurve 5) mit der auf dem Papier beim Gemisch Benzylalkohol-Chlorwasserstoffsäure verglichen. Für die Säule konnte ein formaler Rf-Wert von 0,81 errechnet werden. Auf dem Papier erhielten wir Rf-Werte von 0,76, 0,78 und 0,76.

Wenn auch die Eigenschaften des Trägers maßgebend für den Verlauf der Entmischung sind und die große Ähnlichkeit der Meßwerte zufällig sein kann, so beweist sie dennoch die Möglichkeit des Einsatzes der Papierchromatographie bei der Untersuchung des gegebenen Problems.

Nach der o. a. Methode prüften wir systematisch Gemische aus Aceton, Wasser und Salzsäure. Um gleichzeitig den Einfluß der Papierqualität mit zu erfassen, führten wir die Versuche parallel auf Whatman Papier Nr. 1 und Nr. 3 MM durch.

Wie Abb. 7 zeigt, verschiebt sich die 2. Front in Richtung höherer Rf-Werte, wenn man bei konstanter Salzsäurekonzentration den Wassergehalt auf Kosten des Acetons erhöht.

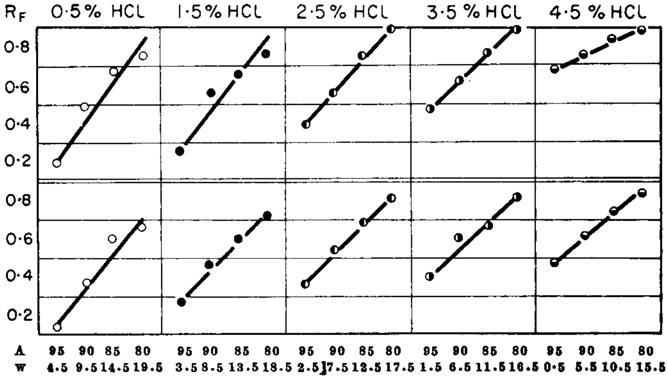


ABB. 7.—Abhängigkeit der Rf-Werte der 2. Front vom Verhältnis Wasser:Aceton bei konstantem Salzsäuregehalt

Hält man den Acetongehalt konstant, dann verschiebt sich die 2. Front zu höheren Rf-Werten mit steigendem Säuregehalt. Die Ergebnisse dieser Versuche sind in Abb. 8 dargestellt.

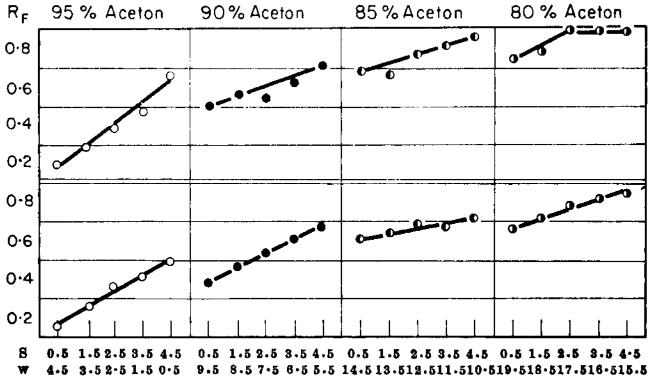


ABB. 8.—Abhängigkeit der Rf-Werte der 2. Front vom Verhältnis Wasser:Salzsäure bei konstantem Acetongehalt.

Aus den Abb. 7 und 8 geht hervor, daß sich die Verhältnisse prinzipiell bei beiden Papiersorten gleichen, daß aber auf der Sorte 3 MM (untere Reihe) die Rf-Werte der 2. Front niedriger liegen.

Diese Versuchsreihe beweist ebenfalls, daß das Fließmittel bei der papierchromatographischen Trennung entmischt wird. Aus den gefundenen Abhängigkeiten geht weiter hervor, daß, wie bei der Säule, die Verhältnisse an der Grenze zwischen mobiler und stationärer Phase nicht durch Bildung einfacher Wasser-Cellulose-Komplexe erklärt werden können. Auch bei der Trennung auf dem Papierbogen nehmen sicher alle Komponenten des Fließmittels am Aufbau der stationären Phase teil.

Es wird Gegenstand weiterer Untersuchungen sein diese Hypothese zu beweisen und die dabei entstehenden Gleichgewichte an der Grenzfläche zwischen Träger und Lösungsmittel zu untersuchen.

Summary—The course of separation of the components of a solvent mixture by the carrier (cellulose or silica gel) has been investigated. By a study of alcohol-water-acid mixtures it has been shown that in partition chromatography the components of the eluting solvent are partially separated, and that the course of the separation depends on the composition of the original solvent mixture. The hypothesis is proposed that at the boundary between the carrier and the solvent system an intermediate layer forms, in which all the compounds of the solvent are present.

Résumé—On a examiné la marche de la séparation des constituants du solvant par le support (cellulose ou gel de silice). Par l'étude de mélanges alcool-eau-acide, on a montré qu'en chromatographie de partage les constituants du solvant d'élution sont partiellement séparés, et que la marche de cette séparation dépend de la composition du mélange solvant initial. On propose l'hypothèse selon laquelle, à la séparation entre le support et le système solvant, il se forme une couche intermédiaire, dans laquelle sont présents tous les constituants du solvant.

LITERATUR

1 C. S. Hanes u. F. A. Isherwood, *Nature*, 1946, **164,** 1107.
2 L. Horner, W. Emrich u. A. Kirschner, *Z. Elektrochem.*, 1952, **56,** 987.
3 E. C. Martin, *J. Chem. Soc.*, 1961, 3935; *J. Chromatog.*, 1963, **10,** 347.
4 R. Krulla, *Z. phys. Chem.*, 1909, **66,** 307.
5 V. Holeyšovský, O. Mjkeš and F. Šorm, *Tschech. Pat.* No. 87674, 15. 10. 1958.

Talanta, 1964, Vol. 11, pp. 451 to 459. Pergamon Press Ltd. Printed in Northern Ireland

ZUR ENTMISCHUNG DER LÖSUNGSMITTEL BEI DER CHROMATOGRAPHISCHEN TRENNUNG—II*

SELEKTIVE SORPTION DER MISCHUNGEN ALKOHOL–WASSER UND ALKOHOL–WASSER–SÄURE AN DER CELLULOSESÄULE

JAN MICHAL und GERHARD ACKERMANN
Institut für Erzforschung Praha, ČSSR und Institut für anorganische und analytische Chemie der Bergakademie Freiberg (Sachsen), DDR

(*Eingegangen am* 17. *Juli* 1963. *Angenommen am* 18. *September* 1963)

Zusammenfassung—Bei der Untersuchung von Gemischen aus Alkohol und Wasser bzw. Alkohol, Wasser und Säure wird festgestellt, daß der Charakter der selektiven Sorption sich in der Reihe der Alkohole und mit steigendem Wassergehalt ändert. Bei Gemischen mit sehr geringem Wasseranteil kommt es in einigen Fällen zu bevorzugter Sorption des Alkohols. Mit steigendem Wassergehalt ändert sich der Charakter der Entmischung und es kann bevorzugte Wasseraufnahme festgestellt werden. Bei den Mischungen Alkohol–Wasser–Säure wurde bewiesen, daß an der Bildung der Zwischenschicht auf der Cellulose auch die Säure beteiligt sein muß. Im Falle des Verhaltens der Mischungen auf lufttrockener Cellulose konnte ein weiteres Argument dafür erhalten werden, daß sich offenbar am Aufbau der Grenzschicht zwischen fester und flüssiger Phase alle Komponenten des Lösungsmittelsystems beteiligen.

IN der 1. Mitteilung[1] haben wir gezeigt, daß aus einem Lösungsmittelgemisch einzelne Komponenten an der Cellulosesäule selektiv festgehalten werden. Auf Grund unserer Meßergebnisse gelangten wir zur Ansicht, daß sich am Aufbau der Grenzschicht zwischen Träger und Fließmittelsystem wahrscheinlich alle Komponenten des Lösungsmittels beteiligen. Es muß vermutet werden, daß dabei Gleichgewichtssysteme entstehen, deren Zusammensetzung von Art und Mischungsverhältnis des Fließmittels bestimmt wird.

Im folgenden soll dieser Entmischungsvorgang an Gemischen aus Alkohol–Wasser bzw. Alkohol–Wasser–Salzsäure näher betrachtet werden. Aus experimentellen Gründen wird dabei zunächst die Aufnahme von Wasser und von Säure in die stationäre Phase untersucht werden.

VERSUCHSANORDNUNG

Es wurden wieder Säulen mit einem Durchmesser von 2,5 cm und einer Höhe von 40 cm verwendet, die stets 35 g Cellulose enthielten. Das Cellulosepulver (Whatman Standard Grade) wurde in der unten beschriebenen Weise vorbehandelt, wobei wir auf genaue Einhaltung der Versuchsbedingungen besonderen Wert legten.

Die benutzten Alkohole reinigten wir durch mehrfache Destillation und bewahrten sie in Flaschen mit Schliffstopfen auf. Den Wassergehalt der Alkohole bestimmten wir wieder durch Titration mit Karl-Fischer-Lösung. Die vorbehandelte Cellulose füllten wir in die Säule bis zur Marke, welche einer Cellulosemenge von 35 g entsprach, ein. Das zu untersuchende Gemisch lief dann wieder mit einer Geschwindigkeit von 1–2 ml/min über die Säule. Das Eluat wurde in Meßzylindern aufgefangen aus denen wir jeweils 2 ml Lösung für die Wasserbestimmung entnahmen.

---

* I. Mitteilung: Literatur Punkt 1.

SYSTEM ALKOHOL–WASSER

Die einfachsten Systeme, welche zum Studium des Entmischungsvorganges der Fließmittel in der chromatographischen Analyse benutzt werden können, sind Gemische der niederen Alkohole mit Wasser. Diese Alkohole sind infolge ihrer Affinität zur Cellulose und der Größe ihrer Dielektrizitätskonstanten aus der großen Reihe der organischen Lösungsmittel, die man in der Verteilungschromatographie benutzt, dem Wasser am nächsten. Sie geben uns durch ihre unbegrenzte Mischbarkeit mit Wasser die Möglichkeit Änderungen an der Grenze zwischen fester und flüssiger Phase unter verschiedenen Bedingungen zu verfolgen.

Das verwendete Cellulosepulver wurde wie folgt vorbehandelt:

(1) 12 Std. bei 110°C im Trockenschrank getrocknet
(2) 12 Std. bei 110°C im Trockenschrank getrocknet und anschließend 12 Std. in wasserdampfgesättigter Atmosphäre aufbewahrt.
(3) 12 Std. bei 110°C im Trockenschrank getrocknet und anschließend 12 Std. dem Dampf des verwendeten Alkohols ausgesetzt.

Methanol-Wasser

Die Mischung wurde mit mehrmals destilliertem reinem Methanol hergestellt. Der Wassergehalt betrug 4,5 mg/ml Methanol.

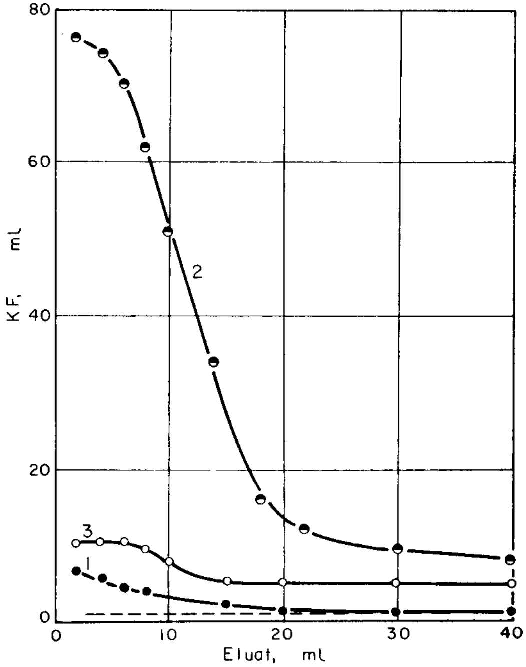


ABB. 1.—Änderung der Wasserkonzentration im Filtrat.
Methanol–Wasser
(1) Cellulose bei 110°C getrocknet.
(2) Cellulose bei 110°C getrocknet und mit Wasserdampf gesättigt.
(3) Cellulose bei 110°C getrocknet und mit Methanoldampf gesättigt.

In Abb. 1 ist die Änderung des Wassergehaltes im Eluat in Abhängigkeit von dessen Gesamtvolumen dargestellt.

Aus der Figur muß man die erstaunliche Tatsache ableiten, daß es bei allen 3 Versuchsreihen zu einer bevorzugten Alkoholaufnahme aus dem Gemisch Methanol-Wasser kommt. Nach dem Durchfluß durch die mit getrockneter Cellulose gefüllte Säule sind die ersten Fraktionen des Eluats reicher an Wasser als die ursprüngliche Mischung. Eine ähnliche Erscheinung war auch an der mit Alkoholdämpfen gesättigten Säule zu beobachten. Der gleiche Effekt trat bei der mit Wasserdampf gesättigten Säule auf, wobei hier der Wassergehalt des Eluats besonders hoch lag. Auf Grund dieser Versuchsreihe ist es allerdings noch nicht möglich zu erklären, ob bei diesen Versuchen das an die Cellulose gebundene oder nur das "freie" Wasser an das Filtrat abgegeben wird.

Äthanol-Wasser

Die Mischung wurde mit mehrmals destilliertem reinem Äthanol hergestellt. Der Wassergehalt betrug 40,2 mg/ml Äthanol.

In Abb. 2 ist wieder die Änderung des Wassergehaltes im Eluat in Abhängigkeit von dessen Gesamtvolumen dargestellt.

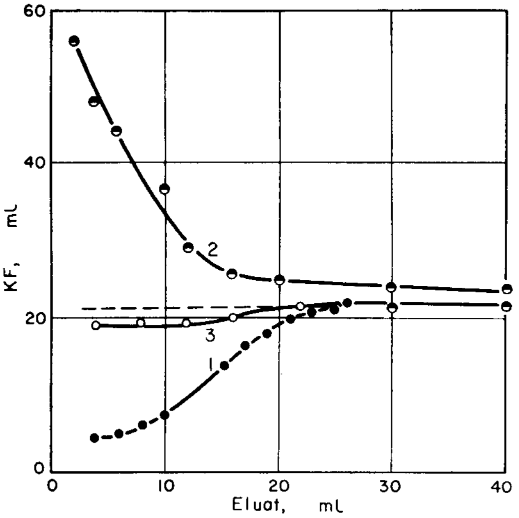


Abb. 2.—Änderung der Wasserkonzentration im Filtrat. Äthanol–Wasser
(1) Cellulose bei 110°C getrocknet.
(2) Cellulose bei 110°C getrocknet und mit Wasserdampf gesättigt.
(3) Cellulose bei 110°C getrocknet und mit Äthanoldampf gesättigt.

Die an der trockenen und mit Alkoholdampf gesättigten Säule erhaltenen Meßwerte sprechen für die bisher gültigen Vorstellungen vom Aufbau eines Cellulose-Wasser-Komplexes, denn die ersten Anteile des Eluats sind wasserärmer als die Ausgangslösung. Bei der mit Wasserdampf gesättigten Säule ist allerdings das Filtrat wie beim Methanol zu Anfang wasserreicher als die Ausgangslösung.

n-Propanol-Wasser

Die Mischung wurde mit reinem mehrfach destilliertem n-Propanol hergestellt. Der Wassergehalt betrug 3,8 mg/ml n-Propanol.

In Abb. 3 ist wieder die Änderung des Wassergehaltes im Eluat in Abhängigkeit von dessen Gesamtvolumen dargestellt.

Der Charakter des Entmischungsvorganges entspricht merkwürdigerweise sowohl auf der trockenen wie auf der mit Wasserdampf gesättigten Säule wieder dem Befund beim Gemisch Methanol–Wasser.

Da diese Unregelmäßigkeit in der Reihe der Alkohole auffallend war, schenkten wir den Bedingungen, unter welchen diese Resultate erhalten worden waren besondere Aufmerksamkeit. Es ist auffallend, daß Methanol und n-Propanol bedeutend wasserärmer sind als das verwendete Äthanol. Es mußte daher kontrolliert werden, ob die Wassermenge in der Ausgangslösung auf den Charakter der bevorzugten Sorption Einfluß hat.

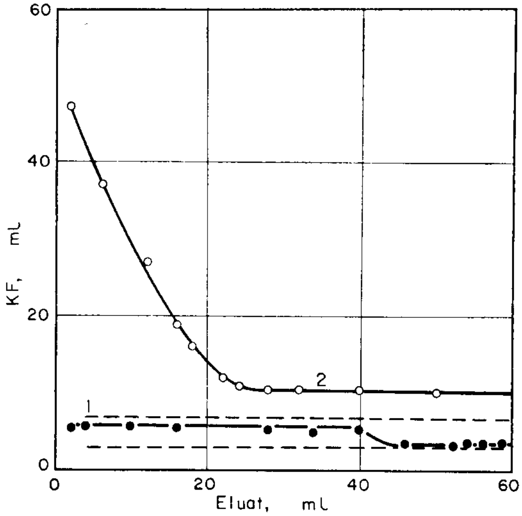


ABB. 3.—Änderung der Wasserkonzentration in Filtrat.
n-Propanol–Wasser
(1) Cellulose bei 110°C getrocknet.
(2) Cellulose bei 110°C getrocknet und mit Wasserdampf gesättigt.

Wir wiederholten deshalb zunächst diese Versuche an der getrockneten Cellulosesäule mit n-Propanol–Wasser–Mischungen, die 3,8 mg bzw. 11,5 mg bzw. 26,5 mg Wasser/ml n-Propanol enthielten. Die Resultate dieser Versuchsreihe sind in Abb. 4 wiedergegeben.

Es muß angenommen werden, daß sich die für das Propanol gefundenen Verhältnisse im Prinzip auch auf die anderen Alkohole übertragen lassen. Weitere Versuche, über die später noch berichtet wird, bestätigen diese Vermutung.

Man kann also feststellen, daß die Zusammensetzung des Fließmittels von bestimmenden Einfluß auf den Charakter der selektiven Sorption der Lösungsmittel für die Cellulose ist. Während es bei Gemischen mit geringem Gehalt an Wasser zur bevorzugten Aufnahme des Alkohols kommt, ändert sich mit steigendem Wasseranteil der Charakter der Kurven und es kommt zur bevorzugten Sorption des Wassers.

SYSTEM ALKOHOL–WASSER–SÄURE

Um die Verhältnisse auch bei komplizierteren Mischungen zu klären, haben wir die ternären Systeme Alkohol–Wasser–Säure studiert. Wir wählten wieder Methanol, Äthanol, Isopropanol (und Benzylalkohol) und—in allen Fällen—Chlorwasserstoffsäure. Die Mischungen waren etwa 0,05 M an Salzsäure und enthielten 50–100 mg Wasser/ml Lösung.

Das verwendete Cellulosepulver wurde wie folgt vorbehandelt:

(1) 12 Std. bei 110°C im Trockenschrank getrocknet
(2) An der Luft bei Zimmertemperatur getrocknet
(3) Lufttrockenes Pulver 12 Std. dem Dampf des verwendeten Alkohols ausgesetzt
(4) Lufttrockenes Pulver 12 Std. dem Dampf des verwendeten Fließmittels ausgesetzt

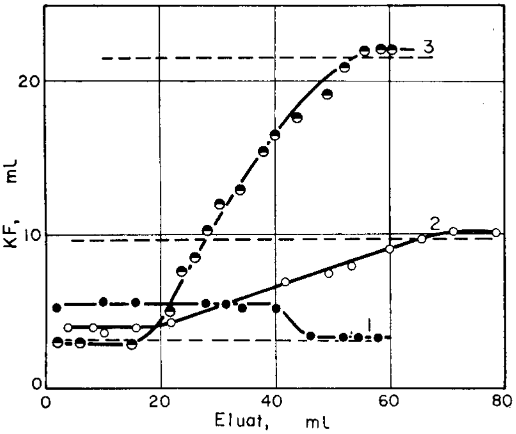


Abb. 4.—Änderung der Wasserkonzentration im Filtrat. n-Propanol–Wasser

(1) Wassergehalt 3,8 mg/ml.
(2) Wassergehalt 11,5 mg/ml.
(3) Wassergehalt 26,5 mg/ml.

In allen Fällen sind wir prinzipiell so vorgegangen, wie wir es beim Studium der Mischungen Alkohol–Wasser beschrieben haben. Das Eluat verwendeten wir abwechselnd einmal zur Wasserbestimmung mit Karl-Fischer-Reagens und zum anderen zur Bestimmung des Säuregehaltes durch Titration mit 0,05 N Natronlauge.

Methanol–Wasser–Chlorwasserstoffsäure

Die Abb. 5 und 6 zeigen die Abhängigkeit des Wasser- bzw. des Säuregehaltes vom Gesamtvolumen des Eluats. Die Diagramme enthalten auch gleichzeitig als gestrichelte Linie Angaben über den Wasser- bzw. Säuregehalt der Ausgangslösung.

Äthanol–Wasser–Chlorwasserstoffsäure

Die Abb. 7 und 8 zeigen die Abhängigkeit des Wasser- bzw. Säuregehaltes vom Gesamtvolumen des Eluats. Die Diagramme enthalten auch gleichzeitig als gestrichelte Linie Angaben über den Wasser- bzw. Säuregehalt der Ausgangslösung.

Isopropanol–Wasser–Chlorwasserstoffsäure

Die Abb. 9 und 10 zeigen die Abhängigkeit des Wasser- bzw. Säuregehaltes vom Gesamtvolumen des Eluats. Die Diagramme enthalten auch gleichzeitig als gestrichelte Linie Angaben über den Wasser- bzw. Säuregehalt der Ausgangslösung.

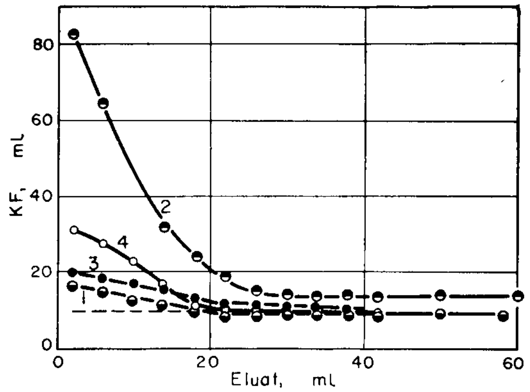


ABB. 5.—Abhängigkeit des Wassergehaltes im Filtrat von dessen Gesamtmenge.
Methanol–Wasser–Salzsäure
(1) Cellulose, bei 110°C getrocknet. (3) Cellulose, lufttrocken, mit Methanoldampf gesättigt.
(2) Cellulose, lufttrocken. (4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

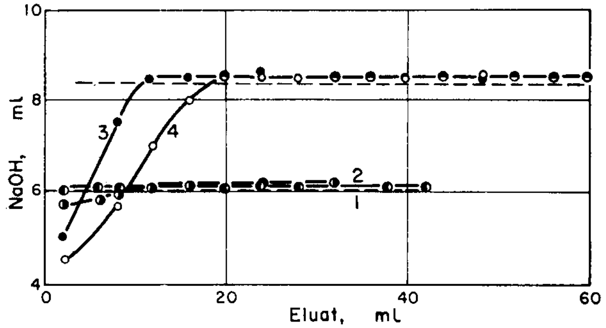


ABB. 6.—Abhängigkeit der Salzsäurekonzentration im Filtrat von dessen Gesamtmenge.
Methanol–Wasser–Salzsäure
(1) Cellulose, bei 110°C getrocknet. (3) Cellulose lufttrocken, mit Methanoldampf gesättigt.
(2) Cellulose, lufttrocken. (4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

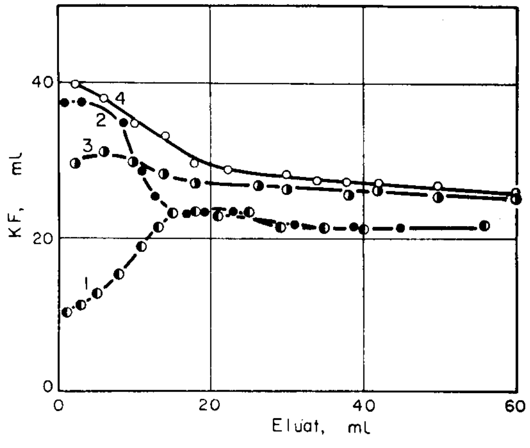


ABB. 7.—Abhängigkeit des Wassergehaltes im Filtrat von dessen Gesamtmenge.
Äthanol–Wasser–Salzsäure
(1) Cellulose, bei 110°C getrocknet. (3) Cellulose, lufttrocken, mit Äthanoldampf gesättigt.
(2) Cellulose, lufttrocken. (4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

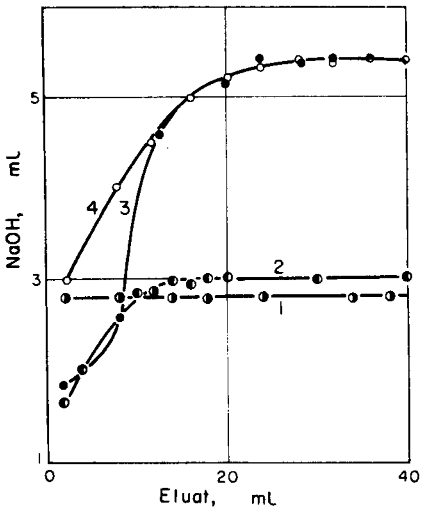


Abb. 8.—Abhängigkeit der Salzsäurekonzentration im Filtrat von dessen Gesamtmenge. Äthanol–Wasser–Salzsäure

(1) Cellulose, bei 110°C getrocknet.
(2) Cellulose, lufttrocken.
(3) Cellulose, lufttrocken, mit Äthanoldampf gesättigt.
(4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

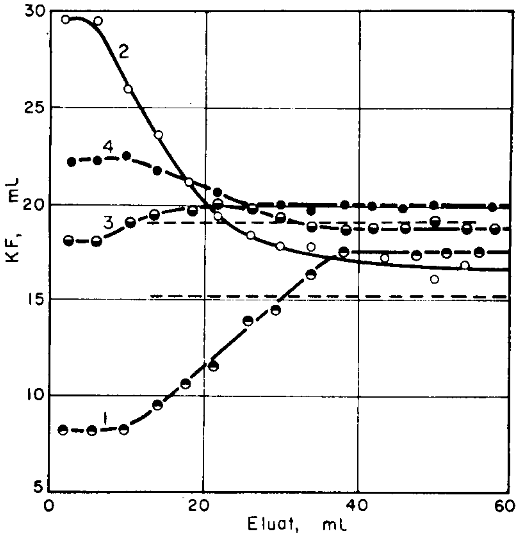


Abb. 9.—Abhängigkeit des Wassergehaltes im Filtrat von dessen Gesamtmenge. i-Propanol–Wasser–Salzsäure

(1) Cellulose, bei 110°C getrocknet.
(2) Cellulose, lufttrocken.
(3) Cellulose, lufttrocken, mit i-Propanoldampf gesättigt.
(4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

Auch bei den untersuchten 3-Komponenten-Systemen können wir beobachten, daß es beim Durchlauf der Lösungsmittelgemische durch die Cellulosesäulen zu einer Veränderung in deren Zusammensetzung kommt. Mit wechselndem Alkohol ändert sich der Charakter der Kurven nicht prinzipiell. Allerdings sind bei den einzelnen Versuchen in den ersten Teilen des Eluats recht unterschiedliche Mengen an Wasser und an Chlorwasserstoffsäure enthalten. Vergleicht man die beiden Serien von Meßreihen miteinander, so kann man erkennen, daß die Veränderung der Salzsäure- und der Wasserkonzentration im Eluat im entgegengesetzten Sinn verlaufen. Eine Ausnahme bildet die bei 110°C getrocknete Cellulose, wo die Salzsäurekonzentration im Eluat konstant bleibt und praktisch der Säurekonzentration in der ursprünglichen Mischung gleicht. In allen anderen Fällen wird Säure von der Säule aufgenommen.

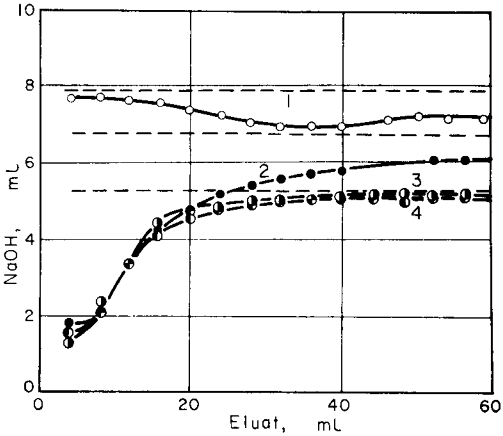


ABB. 10.—Abhängigkeit der Salzsäurekonzentration im Filtrat von dessen Gesamtmenge.

i-Propanol–Wasser–Salzsäure

(1) Cellulose, bei 110°C getrocknet.
(2) Cellulose, lufttrocken.
(3) Cellulose, lufttrocken, mit i-Propanoldampf gesättigt.
(4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

Zu einem interessanten Ergebnis kommen wir noch, wenn wir uns den Wassergehalt der Eluate bei den verschiedenen Alkoholen [Abb. 5, 7 und 9, Kurve (2)] in den Lösungen ansehen, die die bei 110°C getrockneten Säulen passiert haben. Die entsprechenden Kurven sind nochmals in Abb. 11 zusammengefaßt.

Obwohl der Wassergehalt in den untersuchten Gemischen nicht exakt gleich ist, geht aus dem Bild hervor, daß die verschiedenen Alkohole aus der Celluslose unterschiedliche Wassermengen verdrängen. Methanol steht wieder an der Spitze, während aus Benzylalkohol im Gegenteil von der Säule noch Wasser aufgenommen wird.

Da bei allen Versuchen die Cellulose in gleicher Weise präpariert und aufbewahrt wurde, können wir aus den erhaltenen Elutionskurven wieder den Schluß ziehen, daß offensichtlich alle Komponenten des Lösungsmittelsystems an der Oberfläche der Cellulose gebunden werden. Das Verhältnis ist aber nicht nur durch die Konzentrationsverhältnisse der Komponenten in der Ausgangsmischung, sondern auch durch die Eigenschaften der organischen Lösungsmittel bedingt. Bei diesen Versuchen wird das Methanol am stärksten gebunden. Mit ansteigenden Gliedern aus der Reihe der Alkohole fällt dann der Gehalt des an der Oberfläche der Cellulose gebundenen Alkohols.

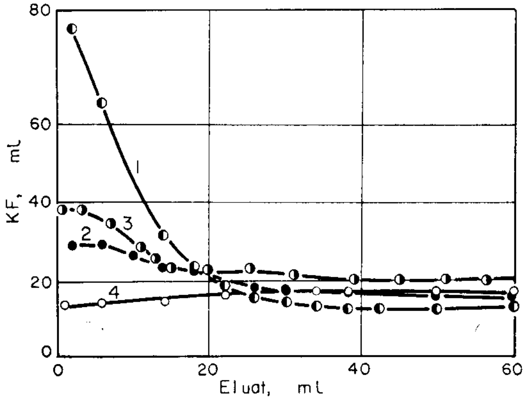


ABB. 11.—Abhängigkeit der Wasserkonzentration im Filtrat bei verschiedenen Alkoholen. Cellulose lufttrocken

(1) Methanol–Wasser–Salzsäure.
(2) Äthanol–Wasser–Salzsäure.
(3) i-Propanol–Wasser–Salzsäure.
(4) Benzylalkohol–Wasser–Salzsäure.

Es muß Gegenstand weiterer Untersuchungen sein diese Abhängigkeit quantitativ zu erfassen und die exakten Verhältnisse an der Grenze zwischen Träger und Lösungsmittel zu untersuchen.

Summary—The character of the selective sorption of alcohol–water and alcohol–water–acid mixtures has been shown to alter on ascending the alcohol series, and with increasing water content. From some mixtures with very low content the alcohol is preferentially sorbed. As the concentration of water increases preferential sorption of water can be shown to occur. For alcohol–water–acid mixtures the acid also participates in the formation of the boundary layer on the cellulose. In the case of air-dried cellulose, it further appears that all the components of the solvent system participate in the formation of the boundary layer between the solid and liquid phases.

Résumé—On a montré que le caractère de sorption sélective de mélanges alcool-eau et alcool-eau-acide est modifié lorsqu'on s'élève dans la série des alcools, et lorsque croît la teneur en eau. A partir de quelques mélanges à très faible teneur en eau, l'alcool est sorbé préférentiellement. Lorsque croît la concentration en eau, on peut montrer qu'il apparaît une sorption préférentielle de l'eau. Pour des mélanges alcool-eau-acide, on a établi que l'acide doit aussi participer à la formation de la couche de jonction sur la cellulose. Dans le cas de la cellulose séchée à l'air, on a acquis un argument supplémentaire quant au fait que tous les constituants du système solvant participent à la formation de la couche de jonction entre les phases solide et liquide.

LITERATUR

[1] J. Michal u. G. Ackermann, *Talanta*, 1964, **11**, 441.

Talanta 1964, Vol. 11, pp. 461 to 469. Pergamon Press Ltd. Printed in Northern Ireland

CYANOMETRIC TITRATIONS IN NON-AQUEOUS SOLUTIONS*

L. Erdey, O. Gimesi and G. Rády
Institute of General Chemistry, Technical University, Budapest XI
Gellért tér 4, Hungary

(*Received* 17 *July* 1963. *Accepted* 21 *October* 1963)

Summary—Elemental sulphur can be titrated directly in a benzene-acetone medium with potassium cyanide dissolved in isopropyl alcohol. A potentiometric or visual indicator (bromothymol blue) end-point can be used. Elemental selenium can be determined by dissolving it in an excess of a standard solution of potassium cyanide in isopropyl alcohol and back-titrating the excess with a standard solution of sulphur in benzene-acetone. Selenium and sulphur can also be determined simultaneously. With these titrants, salts of quaternary ammonium bases, dissolved in a mixture of isopropyl alcohol and acetone, can be titrated.

Our cyanometric titrations in a non-aqueous medium may be divided into three groups: the determination of elemental sulphur, the determination of elemental selenium and the determination of heterocyclic quaternary ammonium salts.

For the determination of elemental sulphur many methods are known. Most methods suggest a preliminary dissolution in acetone or some other solvent for the purpose of separation or enrichment. For the determination of the sulphur content of this extract, gravimetric as well as titrimetric methods are known. A direct titrimetric method in non-aqueous solution has been reported by Skoog and Bartlett.[1] They used acetone as solvent and were able to prepare a $0{\cdot}01F$ solution of sulphur. The titration was carried out with a standard solution of potassium cyanide in isopropyl alcohol. For the determination of substances of higher elemental sulphur content this method could only be used with satisfactory accuracy if a solvent could be found in which sulphur is more soluble than in acetone. For that special purpose we wanted to improve this method and to extend its field of application.

We found that by using benzene and acetone mixed in a ratio of 4 to 1, sulphur solutions may be prepared of $0{\cdot}1F$ concentration. Experience has shown that the sulphur content of sulphur solutions prepared in benzene-acetone mixtures is stable. Consequently, such solutions may be used as standard solutions for the titration of cyanide and indirectly for the determination of elemental selenium.

The titration is based on the fact that cyanide ion, which is a strong Lewis base, is converted to the less basic thiocyanate or selenocyanide ion in the presence of sulphur or selenium; when an excess of cyanide is added there is a sudden increase in the basicity of the solution. On the other hand, when titrating cyanide with standard sulphur solution, the basicity of the solution suddenly decreases at the equivalence point.

In accordance with Skoog and Bartlett,[1] we confirm that bromothymol blue indicates precisely the equivalence point. In order to follow the reaction occurring

---

* Presented at XIXth International Congress of Pure and Applied Chemistry, London, England, 17th July, 1963.

during the titration, we first carried out potentiometric titrations. A 0·1*F* stock solution of sulphur in benzene-acetone, prepared from sulphur recrystallised several times from carbon disulphide and dried at 60°, was titrated with a 0·1*F* standard solution of potassium cyanide in isopropyl alcohol.

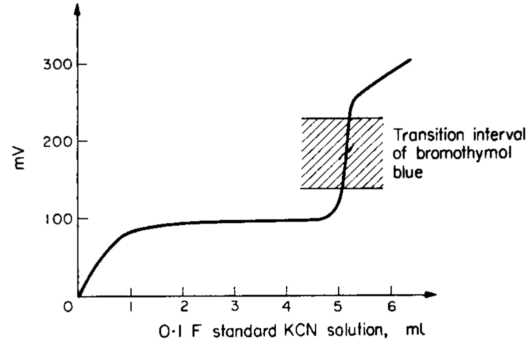


Fig. 1.—Potentiometric titration of a benzene-acetone solution of sulphur with a standard solution of potassium cyanide in isopropyl alcohol.

For the potentiometric titrations a glass indicator electrode and a calomel reference electrode were used, without a salt bridge. This was possible because the small water content of the isopropyl alcohol solution is sufficient for dissolution of the potassium cyanide and at the same time it does not decompose the benzene-containing solution. Twenty-five ml of the sulphur stock solution were titrated with potassium cyanide at 50–60° with magnetic stirring and nitrogen bubbling through the solution. A Metrohm potentiometer was used as the measuring instrument.

Table I.—Titration of a solution of sulphur in benzene-acetone with a standard solution of potassium cyanide in isopropyl alcohol using bromothymol blue as indicator.

KCN consumed, *ml*		Sulphur found, *mg*	Sulphur taken, *mg*	Deviation, %
4·99	0·1*F*	16·00	16·03	−0·18
5·00		16·03	16·03	−0·00
9·92		31·80	32·06	−0·81
9·97		31·99	32·06	−0·22
19·87		63·74	64·13	−0·60
19·95		63·99	64·13	−0·22
9·90	0·01*F*	3·171	3·206	−1·03
9·86		3·161	3·206	−1·40

In order to ascertain the transition interval of bromothymol blue the potentiometric titrations were also carried out in the presence of this indicator. Fig. 1 shows the titration curve thus obtained. Bromothymol blue is seen to change colour at the potential change which corresponds with the equivalence point. Consequently, the titration can also be carried out with visual end-point indication. The results of some titrations with the visual indicator, performed in the same way as the potentiometric titration, are shown in Table I. The deviation from the true value is seen to vary between 0·0 and −0·8% with 0·1*F* potassium cyanide solution, and between −1 and −1·4% with a 0·01*F* solution.

The method was next applied to various technical materials. Thus, to determine the elemental sulphur content of sulphur recovered from gases, after appropriate pretreatment of a weighed sample it was washed with benzene into a volumetric flask. The flask was shaken until dissolution of the sulphur, then diluted to the mark with acetone. Two–three drops of a 0·1% isopropyl alcohol solution of bromothymol blue indicator were added to an aliquot of this stock solution. After warming to 50–60°, it was titrated with potassium cyanide standard solution until the appearance of a blue coloration. In the neighbourhood of the end-point it is advisable to titrate slowly, because the reaction becomes slow and part of the sulphur may remain untitrated. Some results are summarised in Table II.

TABLE II.—DETERMINATION OF THE ELEMENTAL SULPHUR CONTENT OF SULPHURS RECOVERED FROM GASES

0·1*F* KCN consumed, *ml*	Sulphur found, *mg*	Substance taken, *mg*	Sulphur content of substance, %
I (purified sample)			
10·34	33·15	33·17	99·9
11·97	38·38	38·30	100·2
9·25	29·68	29·71	99·9
II (impure sample)			
8·71	27·93	30·25	92·4
9·55	30·63	33·21	92·2
10·49	33·65	36·23	92·8

TABLE III.—DETERMINATION OF THE ELEMENTAL SULPHUR CONTENT OF PLANT PROTECTIVES

Substance	0·05*F* KCN consumed /10 ml, *ml*	Substance taken, *mg*	Sulphur found,		Sulphur present, %
			mg	%	
"Sulfex"	3·62	178·6	58·03	32·49	30–33
	5·55	269·7	88·98	32·99	
	7·71	385·8	123·61	32·04	
"Sulfarol"	2·29	55·6	41·61	74·98	74–75
	14·00	301·2	224·78	74·53	
	16·24	350·0	260·40	74·40	
"Netzschwefel-Pahlberg"	8·21	217·8	131·74	60·49	60–63
	3·94	103·1	63·30	61·40	
	7·91	206·2	126·91	61·55	

We have also determined the elemental sulphur content of various plant protectives, as did Bartlett and Skoog.[1] The sulphur content of the sample may be extracted either by shaking the test sample with benzene in a volumetric flask or by means of an extractor. The latter procedure must be used if a volume correction should be applied because of a large amount of accompanying material. Aliquots of the resulting stock solution were titrated both potentiometrically and with visual end-point indication (bromothymol blue), the results of these titrations being given in Table III.

The data of this table prove that the method is well suited to the determination of the elemental sulphur content of sulphur-containing plant protectives. The method is rapid and the difference between parallel titrations does not exceed ±1%.

TABLE IV.—DETERMINATION OF ELEMENTAL SULPHUR IN SULPHUR-CONTAINING MEDICINAL CARBON (NEOCARBOLAX)

Elemental sulphur present, *mg/pill*	Sulphur found, *mg*	
	Visual end-point	Potentiometric indication
50	50·10	50·11
50	49·75	49·94
50	49·95	49·99
50	50·02	49·98
50	49·98	50·09

The titration with potassium cyanide was also applied to the determination of the elemental sulphur content of sulphur-containing medicinal carbon (Neocarbolax). Because of the high carbon content the titration must be carried out potentiometrically. Visual end-point indication can only be used after filtration. Table IV shows the results of some titrations. The determination is of sufficient accuracy, the greatest observable error being about ±0·2%.

An attempt was made to apply the sulphur titration to the determination of cyanide. A 0·1*F* isopropyl alcohol solution of cyanide was titrated with a 0·1*F* standard sulphur solution in acetone-benzene using both potentiometric and visual end-point indication. The curve of our potentiometric titration carried out by using a glass and a saturated calomel electrode in the presence of bromothymol blue or titan yellow can be seen in Fig. 2 and the results of the titrations carried out in the presence of titan yellow are to be seen in Table V. The standard deviation calculated on the basis of 20 parallel titrations, in which 65 mg of potassium cyanide were taken as test, was ±0·014 ml of 0·1*F* sulphur solution.

TABLE V.—TITRATION OF A 0·1*F* SOLUTION OF POTASSIUM CYANIDE IN ISOPROPYL ALCOHOL WITH A 0·1*F* STANDARD BENZENE-ACETONE SOLUTION OF SULPHUR IN THE PRESENCE OF TITAN YELLOW

0·1*F* Sulphur solution consumed, *ml*	KCN found, *mg*	KCN taken, *mg*	Deviation, %
4·98	32·42	32·56	−0·42
4·96	32·29	32·56	−0·82
4·97	32·36	32·56	−0·61
9·97	64·92	65·12	−0·30
9·95	64·79	65·12	−0·50
9·94	64·72	65·12	−0·61
9·98	64·98	65·12	−0·21
9·95	64·79	65·12	−0·50
Deviation from true value			−0·49

The possibility of titrating potassium cyanide in a non-aqueous solution with a standard solution of elemental sulphur led us to try and extend the method to the determination of selenium. Elemental selenium was found to dissolve easily in an excess of an isopropyl alcohol solution of potassium cyanide to form selenocyanide. The excess cyanide can be titrated with a 0·1*F* standard solution of elemental sulphur to titan yellow or potentiometrically. Some results of the determination of purified selenium are shown in Table VI.

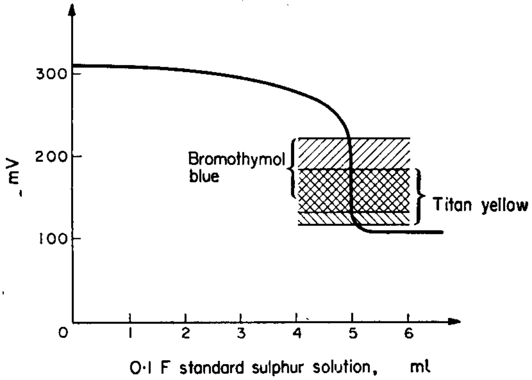


FIG. 2.—Potentiometric titration of a solution of potassium cyanide in isopropyl alcohol with a standard solution of sulphur in benzene-acetone.

TABLE VI.—INDIRECT TITRATION OF PURIFIED SELENIUM WITH A STANDARD SOLUTION OF SULPHUR IN BENZENE-ACETONE

0·1*F* KCN soln. used, *ml*	0·1*F* Sulphur soln. consumed, *ml*	Selenium found, *mg*	Selenium taken, *mg*	Deviation, %
10·00	5·47	35·82	35·60	+0·62
10·00	5·79	33·24	33·10	+0·45
10·00	6·39	28·58	28·39	+0·99
10·00	6·16	30·34	30·65	+1·01
10·00	6·13	30·60	30·45	+0·59

Elemental sulphur and selenium can be determined in the presence of each other, because elemental sulphur dissolves in benzene whereas selenium does not. The dissolved sulphur can be titrated directly with a standard solution of potassium cyanide in isopropyl alcohol. After the whole of the sulphur has been converted to thiocyanate, which may be indicated either visually or potentiometrically, the solid selenium is dissolved in an excess of standard potassium cyanide solution. The excess cyanide solution is then back-titrated with a standard solution of sulphur in benzene-acetone. Fig. 3 shows a potentiometric titration curve obtained with glass and saturated calomel electrodes in the presence of tital yellow. One can observe definite potential changes at the end-point of both reactions. Table VII shows some results of the titration carried out in the presence of titan yellow as indicator. The greatest deviation from the theoretical value is 1·3% for sulphur and +1·0% for selenium.

In a previous method[2] elementary sulphur or selenium was determined by treatment with an excess of potassium cyanide solution, the excess of which was determined by adding excess nickel solution and titrating the uncomplexed nickel with EDTA. It was not possible to determine sulphur and selenium in admixture as in the present method. Furthermore, the present method enables sulphur to be extracted from a sample containing ions which would interfere in a complexometric titration.

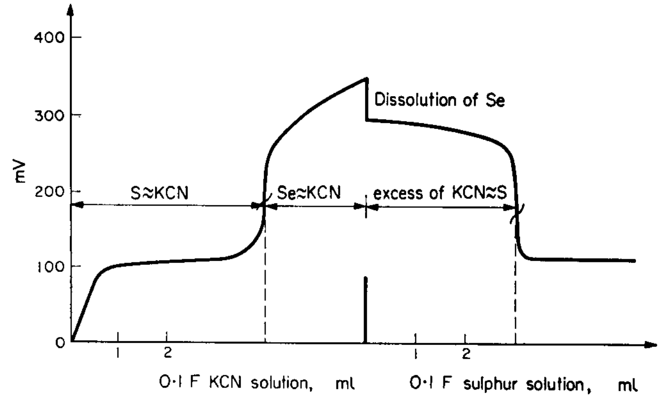
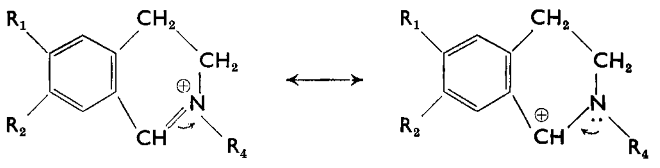


FIG. 3.—Potentiometric titration of elemental sulphur and selenium in the presence of each other.

TABLE VII.—TITRATION OF SULPHUR AND SELENIUM IN THE PRESENCE OF EACH OTHER

Sulphur found, *mg*	Sulphur taken, *mg*	Selenium found, *mg*	Selenium taken, *mg*	Deviation from true value	
				Sulphur, %	Selenium, %
17·86	17·98	28·40	28·34	−0·66	+0·21
17·90	17·98	25·28	25·20	−0·44	+0·35
17·74	17·98	30·30	30·20	−1·33	+0·33
17·85	17·98	29·30	29·00	−0·72	+1·02

It has also been found possible to titrate the salts of heterocyclic quaternary ammonium bases with a standard solution of potassium cyanide in isopropyl alcohol. These salts react quite easily with cyanide ion, the carbon atom next to the quaternary nitrogen atom binding it with a covalent bond. The stability of the resulting cyanide compound depends upon the polarity of the solvent. Heterocyclic quaternary ammonium salts have two mesomeric forms:



quaternary ammonium ion carbonium ion

In polar solvents the quaternary ammonium is the stable form, whereas the non-polar solvents favour the formation of the carbonium ion. The strongly nucleophilic cyanide ion attacks the carbonium ion with the formation of a covalent bond. Because the reaction takes place rapidly and quantitatively, it is well suited for quantitative determinations.

After the heterocyclic quaternary ammonium salt is consumed, the cyanide ion will be in excess and behave in a non-aqueous medium as a strong base. Consequently, the end-point of the titration can be indicated either with acid-base indicators or potentiometrically.

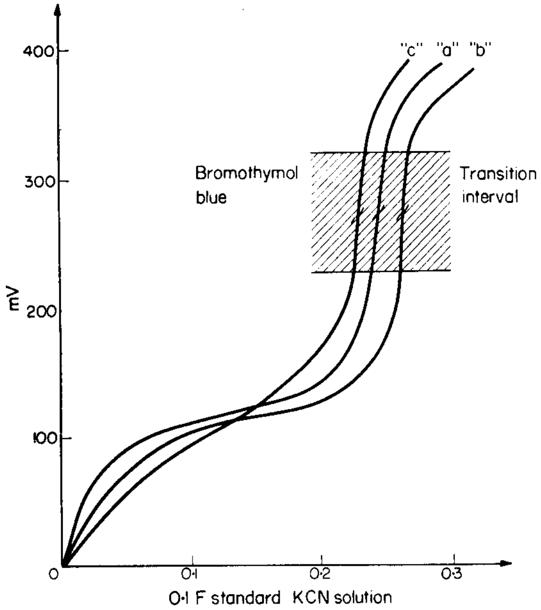
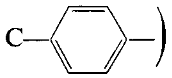


FIG. 4.—Potentiometric titration of heterocyclic quaternary ammonium salts with a standard solution of potassium cyanide in isopropyl alcohol:
(a) cotarnine chloride,
(b) *p*-chlorophenylnorcotarninium chloride,
(c) 2,4-dinitrophenyl-6,7-dimethoxyisoquinolinium chloride.

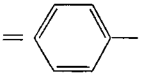
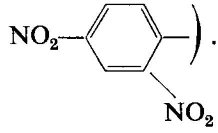
The method was tested by using the following three heterocyclic quaternary ammonium salts:

(a) cotarnine chloride ($R_1 + R_2 = CH_2O_2$, $R_3 = CH_3O$—, $R_4 = CH_3^-$),

(b) *p*-chlorophenylnorcotarninium chloride

($R_1 + R_2 = CH_2O_2$, $R_3 = CH_3O$—, $R_4 =$ ),

(c) 2,4-dinitrophenyl-6,7-dimethoxyisoquinolinium chloride

($R_1 = R_2 = CH_3O$—, $R_3 =$ , $R_4 =$ ).

The substance to be analysed or an aliquot of a previously prepared stock solution was transferred to a titration vessel and the volume adjusted to about 20 ml with a mixture of acetone and isopropyl alcohol (1 : 1). Potentiometric titrations were carried out with a glass and saturated calomel electrode using a 0·1*F* standard solution of potassium cyanide in isopropyl alcohol. Fig. 4 shows the titration curves obtained.

The potentiometric titrations were repeated in the presence of bromothymol blue as indicator. As can be seen, the titration can be carried out with visual end-point indication, because the inflection point of the potentiometric curve coincides with the colour transition of bromothymol blue.

TABLE VIII.—TITRATION OF HETEROCYCLIC QUATERNARY AMMONIUM SALTS WITH A STANDARD SOLUTION OF POTASSIUM CYANIDE IN ISOPROPYL ALCOHOL

Substance	Concentration of standard soln., *F*	Standard soln. consumed, *ml*	Substance found, *mg*	Substance taken, *mg*	Deviation, %
Cotarnine chloride	0·05	0·58	7·4	7·5	−1·3
		0·57	7·3	7·5	−2·6
		1·19	15·2	15·4	−1·3
	0·01	3·13	80·0	80·2	−0·3
p-Chlorophenyl-norcotarninium chloride	0·01	0·95	3·05	3·12	−2·2
		1·91	6·14	6·24	−1·6
	0·05	0·85	15·44	15·60	−1·0
2,4-dinitrophenyl-6,7-dimethoxy-isoquinolinium chloride	0·01	0·78	3·07	3·16	−2·8
		5·41	21·2	21·0	+0·9
	0·01	3·19	62·6	63·0	−0·6
		4·20	82·3	82·4	−0·1

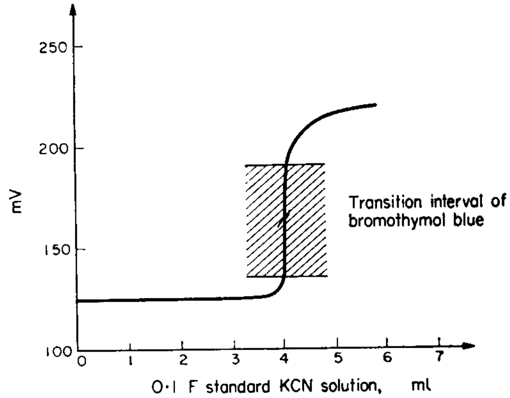


FIG. 5.—Potentiometric titration of cotarnine chloride in the presence of free cotarnine base.

The results of some titrations carried out in the presence of bromothymol blue are summarised in Table VIII. The data show that for titrations performed on the micro scale (10 mg of substance taken and 0·01*F* standard solution used), the error was about 0–3 %, whereas by taking greater amounts of sample, the deviation is only 0·1 %. The standard deviation of the method using 30 mg of substance is ±0·05 ml of 0·05*F* potassium cyanide solution.

It was later found that heterocyclic quaternary ammonium bases in non-aqueous solution do not react with an isopropyl alcohol solution of potassium cyanide. This made it possible to determine quaternary ammonium salts in the presence of their free bases. Fig. 5 shows the curve of the potentiometric titration of cotarnine chloride in the presence of free cotarnine. It is seen from the curve that the medium has a buffer effect and the potential changes only just before the equivalence point giving a definite and well perceptible jump.

In conclusion, a standard solution of potassium cyanide in isopropyl alcohol is seen to be well suited to the titration of many substances. We have succeeded in extending the field of its application for the titration of elemental sulphur. Furthermore, new methods have been developed for the determination of elemental selenium and heterocyclic quaternary ammonium salts. By the last method it is also possible to follow the formation of quaternary salts from the corresponding free bases.

Zusammenfassung—Elementarer Schwefel kann in einer Benzol-Aceton-Lösung mit in Isopropanol gelöstem Kaliumcyanid direkt titriert werden. Es kann potentiometrische oder visuelle (Bromthymolblau) Endpunktsanzeige verwendet werden. Elementares Selen kann bestimmt werden durch Lösen in einem Überschuß eingestellter Kaliumcyanidlösung in Isopropanol und Rücktitration mit einer eingestellten Schwefellösung in Benzol-Aceton. Selen und Schwefel können auch nebeneinander bestimmt werden. Mit diesen Titranten können auch Salze heterocyclischer quartärer Ammoniumbasen, gelöst in Isopropanol-Acton, titriert werden.

Résumé—On peut doser directement le soufre élémentaire en milieu benzène-acétone au moyen de cyanure de potassium en solution dans l'isopropanol. Le point final peut être déterminé potentiométriquement ou au moyen d'un indicateur visuel (bleu de bromothymol). Le sélénium élémentaire peut être dosé par dissolution dans un excès d'une solution titrée de cyanure de potassium en isopropanol, et dosage en retour de l'excès par une solution titrée de soufre dans un mélange acétone-benzène. On peut aussi doser simultanément le sélénium et le soufre. Au moyen de ces solutions titrées, on peut doser des sels de bases hétérocycliques à fonction ammonium quaternaire, dissous dans un mélange isopropanol-acétone.

REFERENCES

[1] D. A. Skoog and J. K. Bartlett, *Analyt. Chem.*, 1955, **27**, 369.
[2] O. Gimesi, G. Rády and L. Erdey, *Acta Chim. Acad. Sci. Hung.*, 1962, **33**, 381.

Talanta, 1964, Vol. 11, pp. 471 to 479. Pergamon Press Ltd. Printed in Northern Ireland

INVESTIGATION OF REAGENTS FOR THE COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF CYANIDE—I

L. S. BARK and H. G. HIGSON
Department of Chemistry and Applied Chemistry, Royal College of Advanced Technology, Salford 5, Lancashire, England

(*Received* 26 *July* 1963. *Accepted* 13 *September* 1963)

Summary—The König synthesis of pyridine dyestuffs by reaction of cyanogen bromide and suitable aromatic amines with pyridine, used as the basis of standard British and American colorimetric methods for the determination of small amounts of cyanide, is reinvestigated. After consideration of the carcinogenic properties of amines capable of being used in a method for cyanide, *p*-phenylenediamine is selected for further examination.

A REVIEW[1] of methods available for the determination of small amounts of cyanide indicates that the colorimetric determination is far superior to others, including titrimetric, polarographic and chromatographic methods. The standard methods for trade wastes and effluents[2,3,4,5] and for waters[4,6] are based either on the colorimetric procedure developed by Aldridge[7,8] or on that of Epstein,[9] which themselves are based on the König reaction[10,11] for the synthesis of pyridine dyestuffs. The latter are formed by reaction of cyanogen bromide or chloride with pyridine and an aromatic amine. Aldridge's method utilises a pyridine/benzidine mixture reacting with cyanogen bromide; Epstein uses cyanogen chloride reacting with pyridine/1-phenyl-3-methyl-5-pyrazolone and a small amount of bis-(1-phenyl-3-methyl-5-pyrazolone). Other workers[12] have used a variation of the Aldridge procedure employing barbituric acid in place of benzidine.

The pyridine/pyrazolone colour development requires the preparation of a relatively unstable reagent, whilst the benzidine method has the distinct disadvantage that the aromatic amine is a well known active carcinogen and the developed colour only obeys Beer's law up to concentrations of the order of 1–2 μg/ml so that it cannot be used for effluents containing more than 2 ppm of cyanide in the measured sample. The barbituric acid method requires a relatively large sample (25 ml) and a relatively long period of heat treatment (40 min at 40°); furthermore, the reagent becomes discoloured on standing for short periods of time.

In view of these criticisms it was decided to reinvestigate the König synthesis as the basis of a method for the determination of cyanide, examining aromatic amines in addition to those considered by König for colour production, and heterocyclic amines other than pyridine as the parent reagent for dyestuff formation.

Examination of heterocyclic amines other then pyridine in the König synthesis

Replacement of pyridine by other heterocyclic amines and their reaction with benzidine and cyanogen bromide (produced from 1 μg of cyanide) produced the results shown in Table 1.

TABLE I

Amine	Colour obtained
Pyridine	Red
Piperidine	None
Morpholine	None
Piperazine	None
Quinoline	None
Isoquinoline	None
2,6-Lutidine	None
α-Picoline	Golden yellow

Apart from pyridine, only α-picoline produced a colour and in this case a much lower maximum absorbance was obtained. Pyridine is, therefore, the best common heterocyclic amine to use.

Examination of aromatic amines other than benzidine in the König synthesis

König synthesised dyes from a number of aromatic amines using pyridine and relatively large quantities of cyanogen bromide. Goris and Larsonneau[13] utilised this reaction for the characterisation of small amounts of pyridine, using aniline as the aromatic amine. One drop of pyridine, 1 drop of aniline and 50–100 mg of cyanogen bromide in 1–20 ml of water, when mixed, yield an intense red colour and a crystalline precipitate; but with traces of pyridine a yellow colour is first produced, which changes after 30–40 min to an orange colour. Přibyl[14] used benzidine instead of aniline for the determination of small amounts of pyridine in aromatic hydrocarbons, measuring the extinction of the solutions at 518 mμ. With only traces of cyanogen bromide, some amines produce different colours from those of the dyes originally synthesised by König. Accordingly, a number of amines were substituted for benzidine in the Aldridge procedure, and the colours produced by reaction with 1 μg of cyanide (as cyanogen bromide) were compared to the corresponding colours of the dyes reported by König (see Table II).

TABLE II

a. *Benzene derivatives*

Number	Amine	Colour of dye	
		As reported by König	Aldridge procedure
1	Aniline	Orange	Yellow, changing to orange (20 to 30 min)
2	*p*-Toluidine	Orange	Yellow, changing to orange (20 to 30 min)
3	*p*-Chloraniline	Orange	Yellow changing to orange (20 to 30 min)
4	*p*-Nitro-aniline	Orange	None detected

TABLE II (*continued*)

b. *Naphthalene derivatives*

Number	Amine	Colour of dye	
		As reported by König	Aldridge procedure
5	*o*-Anisidine	Salmon-pink, with yellowish-red fluorescence	Orange
6	*p*-Phenetidine	Rose-red	Orange, changing to pink
7	*o*-Aminophenol	Rose-red	None detected
8	*p*-Aminophenol	Rose-red	Yellow, changing to orange (20 to 30 min)
9	Anthranilic acid	Bright red, with yellowish-red fluorescence	Yellow, changing to pink (20 to 30 min); fading always occurs
10	Sulphanilic acid	Orange, with greenish fluorescence	Yellow
11	*p*-Aminobenzoic acid	Red	Yellow
12	*o*-Phenylenediamine	Red	Orange (detectable only by spectrophotometer)
13	*m*-Phenylenediamine	Red	None detected (reagent too strongly coloured; evidence of reaction when diluted 125 times)
14	*p*-Phenylenediamine	Red	Cherry-red
15	*p*-Bromo-aniline	—	Yellow
16	α-Naphthylamine	Rose-red	Yellow
17	β-Naphthylamine	Rose-red	Yellow, changing to orange

c. *Amino-azo-compounds*

18	Amino-azobenzene	Heliotrope	None detected

d. *Benzidine derivatives*

19	Benzidine	Lilac	Red
20	*o*-Dianisidine	Blue-violet	Red

TABLE II (*continued*)

e. *Miscellaneous amines not used by König*

Number	Amine	Aldridge procedure colour
21	*p*-Aminodiphenylamine	Cherry-red
22	*p*-Amino-*N*,*N*-dimethylaniline	Red
23	*p*-Acetamido-aniline	Yellow (fades during 10 to 20 min)
24	*p*-Amino-acetophenone	Yellow (fades during 20 to 20 min)
25	4,4′-Diaminodiphenylene oxide	Yellow (fades)
26	*N*-Benzyl-*p*-phenylenediamine	Yellow (fades)
27	*N*-(4-Aminophenyl)piperidine	Yellow[a]
28	*N*-(2-Aminophenyl)piperidine	Yellow[a]
29	*N*-(4-Aminophenyl)pyrrolidine	None detected (red solutions)
30	*N*-(2-Aminophenyl)pyrrolidine	Yellow[a]
31	*N*-(4-Aminophenyl)morpholine	Red
32	*N*-(2-Aminophenyl)morpholine	Yellow (fades rapidly)[a]
33	*N*-(4-Aminophenyl)piperazine	Orange
34	*N*-(2-Aminophenyl)piperazine	None detected (green solutions)
35	Diphenylamine	None detected
36	*p*-Cyclohexylaniline	Yellow, changing to pink (fades)
37	3-Amino-4-cyclohexylaniline	Yellow, changing to orange (fades)
38	4-Aminophenazone	Yellow (fades)
39	Rosaniline	Impossible to detect[b]
40	*N*-(1-Naphthyl)ethylenediamine	None detected
41	Benzylamine	None detected
42	2-Piperidino-3-aminopyridine	None detected
43	2-Pyrrolidino-3-aminopyridine	None detected
44	2-Morpholino-3-aminopyridine	None detected
45	3-Amino-4-morpholinopyridine	None detected
46	2-Aminopyridine	None detected

[a] Certain amines (Nos. 27, 28, 30, 32) only show evidence of reaction with 50 and 100 µg of cyanide (as cyanogen bromide).

[b] With a strongly coloured amine (No. 39), the initial solution is intensely coloured and reaction with 100 µg of cyanide is impossible to detect even at great dilution of the amine solution.

In every case where a yellow colour is produced initially, fading always occurs. Where an orange or red colour is obtained, fading is not so apparent. Therefore, from the amines investigated only *o*-anisidine, *p*-phenetidine, *p*-phenylenediamine, benzidine, *o*-dianisidine, *p*-aminodiphenylamine, *p*-amino-*N*,*N*′-dimethylaniline, *N*-(4-aminophenyl)morpholine and *N*-(4-aminophenyl) piperazine are worth further consideration. For comparison purposes 3-amino-4-cyclohexylaniline was also examined.

By dilution with cyanide-free water of a suitable stock solution, previously standardised with silver nitrate by potentiometric titration and by titration using *p*-dimethylaminobenzylidenerhodanine as indicator, the following 6 cyanide solutions were prepared for each of the 10 amines: (i) 0·0 µg, (ii) 0·1 µg, (iii) 0·2 µg, (iv) 0·5 µg, (v) 1·0 µg, and (vi) 2·0 µg of CN^-. These were examined using a method similar to the Aldridge procedure, the alkaline solutions of cyanide being acidified with 0·6 ml of glacial acetic acid, treated with 0·2 ml of saturated bromine water, mixed thoroughly, excess bromine in the solution removed with 0·2 ml of arsenious acid (2% w/v in water, refluxed until solution is complete) and bromine vapour in the tube removed by air. Before addition of mixed amine/pyridine reagent, the volume of solution was adjusted to 50·0 ml and a 5·0 ml-aliquot taken for the rest of the procedure.

Cyanide solution (v) was examined first in every case. A freshly prepared mixture of 3·0 ml of pyridine reagent (1 litre of 60% w/w aqueous pyridine plus 100 ml of concentrated hydrochloric acid) and 1·0 ml of amine reagent (0·1 g of amine dissolved in 50 ml of 0·5*M* hydrochloric acid; where difficulty was experienced in effecting solution, the mixture was heated to boiling point, cooled and filtered) was added and the absorbance of the solution measured between 450 and 550 mµ at different time intervals using a recording spectrophotometer to ascertain a suitable wavelength to use for each amine reagent. The other test solutions were then treated with the relevant mixed pyridine/amine solutions and the absorbances measured at the appropriate wavelength for each amine reagent, after 20 and 30 min, using a manual spectrophotometer. In most cases the wavelength chosen was that wavelength at which the spectral curve after 30 min crossed the spectral curve after 20 min (isosbestic point). The relatively low concentration of the amine reagent (0.2%) was chosen to enable some amines which were themselves highly coloured in more concentrated solution, to be included in any comparison tests. The same concentration was also used for the benzidine reagent.

Further tests were made altering the conditions simultaneously as follows:

1. The concentration of the amine reagent was increased to 1·0% for amines Nos. 1, 5, 6, 7 and 10.
2. The solutions containing cyanide were arranged so that a volume of 1·0 ml contained the cyanogen bromide before addition of mixed pyridine/amine reagent.

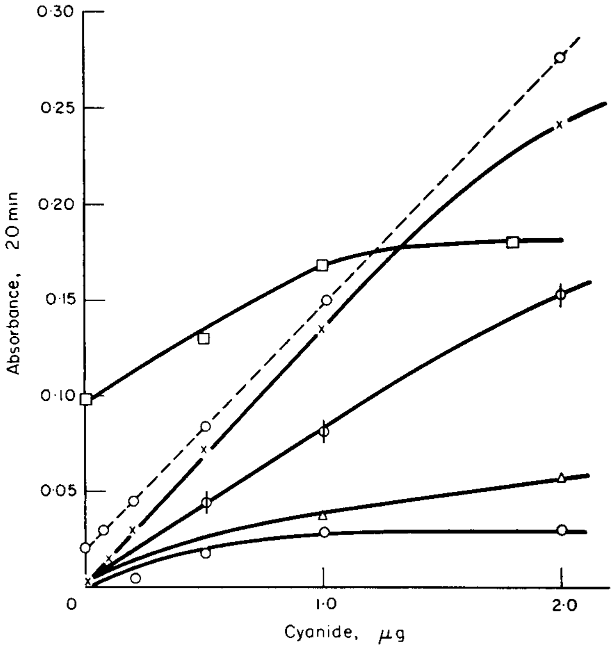


Fig. 1—Calibration curves using 0·2% amine reagents:
——×—— benzidine,
——○—— *o*-anisidine,
——△—— *o*-dianisidine,
——□—— *p*-amino-*N*,*N*-dimethylaniline,
——⏀—— *p*-phenetidine,
– – –○– – – *p*-phenylenediamine.

The results obtained with the 0·2 and 1·0% amine reagents are given in Tables III and IV, respectively, and the corresponding calibration curves in Figs. 1–3.

It appears that a number of amines would be satisfactory for the determination of concentrations of cyanide between 0·1 and 1·0 μg. For more concentrated cyanide solutions, however, the number of amines is restricted. The best amines are benzidine, *p*-phenylenediamine and *p*-aminodiphenylamine. Using the stated conditions and a concentration of 0·2% amine in 0·5*M* hydrochloric acid, *p*-phenylenediamine is the best of the three. At a higher amine concentration (1·0%), benzidine produces the most intense colour and has an absolute absorbance of 0·636 (2·0 μg of cyanide/1·0 ml test solution), whereas *p*-phenylenediamine has an absolute absorbance of only 0·540 but gives a better calibration curve than does benzidine (see Fig. 3). It was necessary at this junction to consider the carcinogenic properties of the amines.

Carcinogenic hazards of aromatic amines

The carcinogenic properties of benzidine are well known. Related compounds, such as 3,3′-dihydroxybenzidine, tetramethylbenzidine and dichlorobenzidine, and other binuclear compounds like 4-aminodiphenyl, 2,3-dimethyl-4-aminodiphenyl and

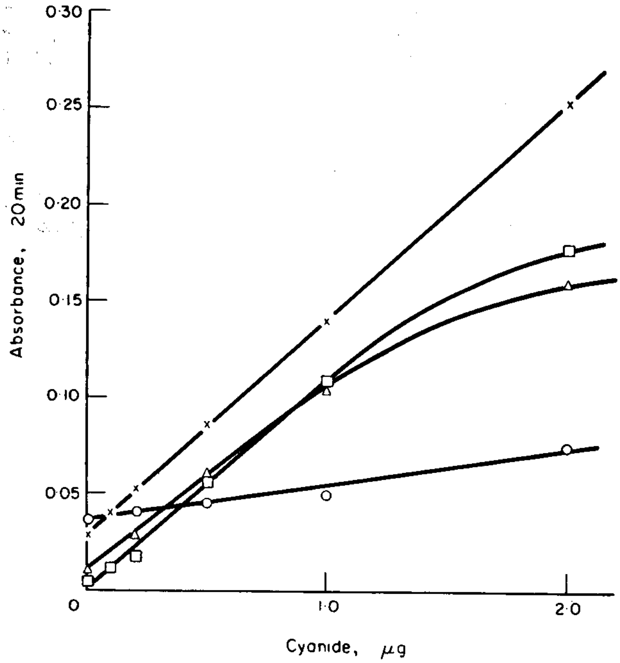


Fig. 2.—Calibration curves for 0·2% amine reagents:
——×—— *p*-amino-diphenylamine,
——○—— *N*-(4-aminophenyl) piperazine,
——□—— 3-amino-4-cyclohexyl-aniline,
——△—— *N*-(4-aminophenyl) morpholine.

Fig. 3—Calibration curves for 1·0% amine reagents:
——○—— benzidine,
——□—— *p*-phenylenediamine,
——△—— *p*-phenetidine,
——×—— *p*-aminodiphenyl-amine.

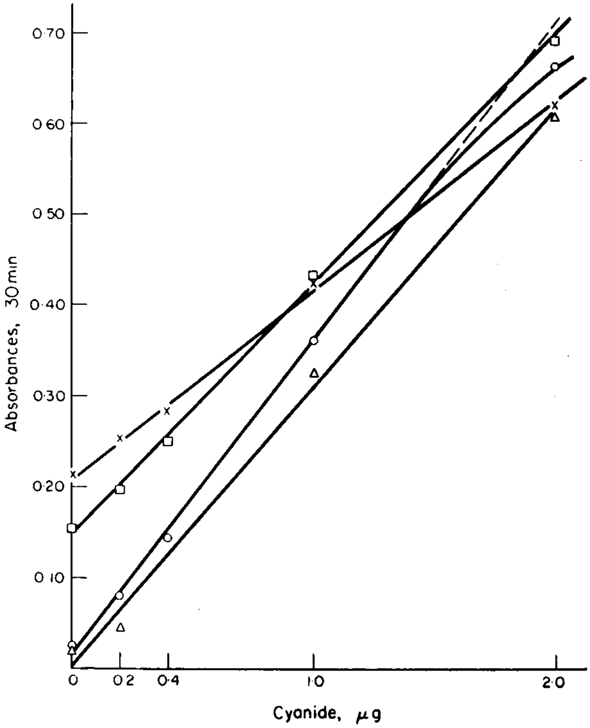


TABLE III—0.2% amine reagent

No.	Amine	Wavelength, *mμ*	Time after mixing, *min*	Absorbance referred to water						Observations
				Cyanide[a], μg						
				0·0	0·1	0·2	0·5	1·0	2·0	
1	Benzidine	522 (isosbestic)	20 30	0·004 0·003	0·015 0·017	0·031 0·034	0·071 0·076	0·135 0·140	0·241 0·251	Good calibration curve (Fig. 1)
2	*o*-Anisidine	508 (isosbestic point)	20 30	0·000 0·000	0·001 0·000	0·005 0·004	0·018 0·016	0·029 0·025	0·031 0·024	Yellow colour fades badly (Fig. 1)
3	*o*-Dianisidine	548	20 30	0·000 0·000	0·006 0·008	0·010 0·010	0·023 0·023	0·039 0·039	0·056 0·051	Similar to *o*-anisidine (Fig. 1)
4	*p*-Amino-*N*,*N*-dimethylaniline	528	30	0·099			0·136	0·169	0·180	Reagent blank highly coloured (Fig. 1)
5	*p*-Phenetidine	510 (peak maximum)	20 30	0·000 0·000	0·005 0·005	0·015 0·015	0·046 0·051	0·089 0·086	0·151 0·159	Yellow colour turns to pink tint and change increases with time (Fig. 1)
6	*p*-Phenylenediamine	508 (isosbestic point)	20 30	0·021 0·026	0·029 0·033	0·044 0·047	0·084 0·089	0·150 0·154	0·273 0·277	Better calibration curve than benzidine (obeys Beer's law better; Fig. 1)
7	*p*-Amino-diphenylamine	541 (isosbestic point)	20 30	0·029 0·032	0·041 0·043	0·052 0·058	0·087 0·093	0·140 0·147	0·252 0·264	Good calibration curve (Fig. 2)
8	*N*-(4-Aminophenyl)-morpholine	517	20 30	0·011 0·015	0·021 0·025	0·029 0·032	0·061 0·064	0·107 0·110	0·159 0·154	Fading at 2.0 μg of cyanide (Fig. 2)
9	N-(4-Aminophenyl)-piperazine	500	20	0·035	0·038	0·042	0·044	0·049	0·073	Poor sensitivity (Fig. 2)
10	3-Amino-4-cyclohexylaniline	504 (isosbestic point)	20 30	0·005 0·006	0·011 0·013	0·021 0·023	0·046 0·057	0·109 0·108	0·176 0·169	Fading at 2.0 μg of cyanide (Fig. 2)

[a] Volume of final mixture of reagents: 9·0 ml.

TABLE IV—1·0% amine reagent[a]

No.	Amine	Wavelength, *mμ*	Time after mixing, *min*	Absorbance referred to water				
				Cyanide[b], μg				
				0·0	0·20	0·40	1·0	2·0
1	Benzidine	510 (isobestic point)	20	0·027	0·080	0·139	0·359	0·663
			30	0·026	0·080	0·139	0·359	0·662
			40	0·029	0·080	0·139	0·358	0·665
5	*p*-Phenetidine	510 (peak maximum)	20	0·018	0·040	—	0·321	0·600
			30	0·021	0·041	—	0·323	0·611
			40	0·021	0·043	—	0·322	0·611
6	*p*-Phenylene-diamine	515 (peak maximum)	20	0·114	0·163	0·255	0·408	0·673
			30	0·152	0·197	0·250	0·432	0·692
			40	0·189	0·231	0·383	0·463	0·718
7	*p*-Amino-diphenylamine	509 (isobestic point)	20	0·186	0·230	0·262	0·413	0·599
			30	0·212	0·248	0·248	0·423	0·618
10	3-Amino-4-cyclohexylaniline	515	30	0·072	0·120	—	0·381	—
10	3% Amine solution	515 (peak maximum)	20	0·222	—	0·335	0·490	0·818
			30	0·238	—	0·352	0·505	0·839
			40	0·247		0·362	0·509	0·853

[a] Absorbances after 30 min are recorded in Fig. 3 for amines 1, 5, 6 and 7.
[b] Volume of final mixture of reagents: 5·0 ml.

naphthalene derivatives, such as 1-amino-2-naphthol, 2-amino-1-naphthol, α-naphylamine and β-naphthylamine, have been reported as being highly active.[15] Dianisidine and the tolidines are suspected of being carcinogenic.

Because there is no published evidence that amines with only a single ring are active, it was decided to confine further investigations to *p*-phenylenediamine.

Zusammenfassung—Die Farbstoffsynthese nach König, die Reaktion von Bromcyan nit geeigneten Aminen, die britischen und US-Standardmethoden zugrundeliegt, wird an 46 Aminen unter geeigneten Bedingungen nachgeprüft. Nach Erörterung der carcinogenen Eigenschaften von Aminen, die zur analytischen Bestimmung kleiner Cyanidmengen geeignet sind, wurde *p*-Phenylendiamin zur weiteren Untersuchung gewählt.

Résumé—Les auteurs ont repris l'étude de la synthèse de König des colorants dérivés de la pyridine, par action du bromure de cyanogène et d'amines aromatiques appropriées sur la pyridine, sur laquelle sont fondées les méthodes colorimétriques étalons britannique et américaine de détermination de petites quantités de cyanure. Tenant compte des propriétés cancérigènes des amines susceptibles d'être utilisées dans une telle méthode, ils ont choisi a p-phenylènediamine pour une étude plus poussée.

REFERENCES

[1] L. S. Bark, *Ind. Chemist*, 1962, 525.

[2] Joint Committee of Association of British Chemical Manufacturers and Society for Analytical Chemistry, *Recommended Methods for the Analysis of Trade Effluents.* W. Heffer and Sons Ltd., Cambridge, 1958.

[3] Society for Analytical Chemistry, *Official Standardised and Recommended Methods of Analysis.* W. Heffer and Sons Ltd., Cambridge, 1963, p. 253.

[4] American Public Health Association, American Water Works Association and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Waste Water.* 11th Edition, Parts III and IV, 1960.

[5] Ministry of Housing and Local Government, *Methods of Chemical Analysis Applied to Sewage and Effluents.* Her Majesty's Stationery Office, London, 2nd Edition, 1956.

[6] Joint Committee of Institution of Water Engineers, Royal Institute of Chemistry, Society for Analytical Chemistry and Society for Water Treatment and Examination, *Approved Methods for the Physical and Chemical Examination of Water.* Institution of Water Engineers, London, 2nd Edition, 1960.

[7] W. N. Aldridge, *Analyst*, 1944, **69**, 262.

[8] *Idem, ibid.*, 1945, **70**, 474.

[9] J. Epstein, *Analyt. Chem.*, 1947, **19**, 272.

[10] W. König, *J. prakt. Chem.*, 1904, **69**, 105.

[11] *Idem, Z. angew. Chem.*, 1905, 115.

[12] G. V. L. N. Murty and T. S. Viswanathan, *Analyt. Chim. Acta*, 1961, **25**, 293.

[13] A. Goris and A. Larsonneau, *Bull. Sci. Pharmacol.*, 1921, **28**, 497.

[14] M. Přibyl, *Coll. Czech. Chem. Comm.*, 1962, **27**, 1330; *Analyt. Abs.*, 1962, **9**, 5267.

[15] T. S. Scott, *Carcinogenic and Caronic Toxic Hazards of Aromatic Amines.* Elsevier Publishing Company, Amsterdam, 1962.

Talanta, 1964, Vol. 11, pp. 481 to 484. Pergamon Press Ltd. Printed in Northern Ireland

CHELATING RADIOMETRIC TITRATIONS BY ION EXCHANGE FOR DETERMINATION OF TRACES OF METALS

JIŘÍ STARÝ, JAROMÍR RŮŽIČKA and ADOLF ZEMAN
Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics
Praha 1, Břehová 7, Czechoslovakia

(*Received* 29 *July* 1963. *Accepted* 13 *October* 1963)

Summary—A new type of radiometric titration has been developed. Using EDTA solutions, the negatively charged or neutral metal chelates are formed, and these can easily be separated from the excess of unreacted metal ions using a cation exchanger. Titration curves are constructed from the activities of the eluates. The method has been used for the determination of microgram amounts of indium using ^{114m}In as an isotopic tracer, and for the determination of submicrogram traces of cobalt using the same indicator as a non-isotopic tracer.

IN radiometric titrations the radiotracer is involved in the chemical reaction which is the basis of the determination. The compound formed during the titration must be easily separated from the excess of the unreacted ions and the end-point is determined from the change in the activity of the residual solution or of the other phase. Two types of radiometric titration have previously been described. In precipitation titrations the second phase is a precipitate, and the end-point can be determined by the appearance of the activity in the aqueous phase, or by its disappearance from the aqueous phase, according to circumstances.[1] Precipitation titrations are difficult to apply, because of the necessity for handling precipitates, to less than milligram amounts and impossible at the submicrogram level.

Extractive titrations[2,3] are based on the formation of metal chelates which can be separated from the unreacted metal ions by solvent extraction. The end-point is determined similarly from the change in activity either of the aqueous phase or of the organic phase. This type of titration is far more sensitive, but has been applied only to a limited number of determinations.

In the present paper a new type of radiometric titration using EDTA is proposed and its utility is verified.

RADIOMETRIC TITRATIONS USING EDTA

EDTA titrations are widely used for determination of many metals, but their sensitivity is limited by the sensitivity of the determination of the end-point. However, using radiometric indication the determination of submicrogram amounts of metals can be carried out without difficulty.

Radiometric titrations using EDTA are based on the formation of negatively charged or neutral chelates which can easily be separated from the excess of the unreacted metal ions on a cation exchanger. The end-point is determined from the activities of the eluates obtained. As in other radiometric titrations, isotopic or non-isotopic tracers can be used. In the first case the radioactive indicator is a radioisotope of the element being determined. In the second case the titration of the element to be assayed is followed by means of an element which is chelated after all the metal being determined is bonded in the EDTA complex (*i.e.* the stability constant of the complex of the radioactive tracer with EDTA is much lower than that of the metal to be determined).

The optimum pH for the titration can be calculated from the basic theory given in our paper on isotope dilution by ion exchange.[4] From this theory it follows that the determination of metals forming very stable chelates (*e.g.*, Co^{III}, Zr^{IV}, Fe^{III}, In^{III}, Th^{IV}, *etc.*[5]) can be carried out at pH 2–3 using 10^{-6}–10^{-7} *M* EDTA solutions. The pH for the determination of metals having lower stability constants must, however, be much higher.

This method has been applied to the determination of microgram amounts of indium by means of an isotopic tracer, and to the determination of traces of cobalt using a non-isotopic tracer.

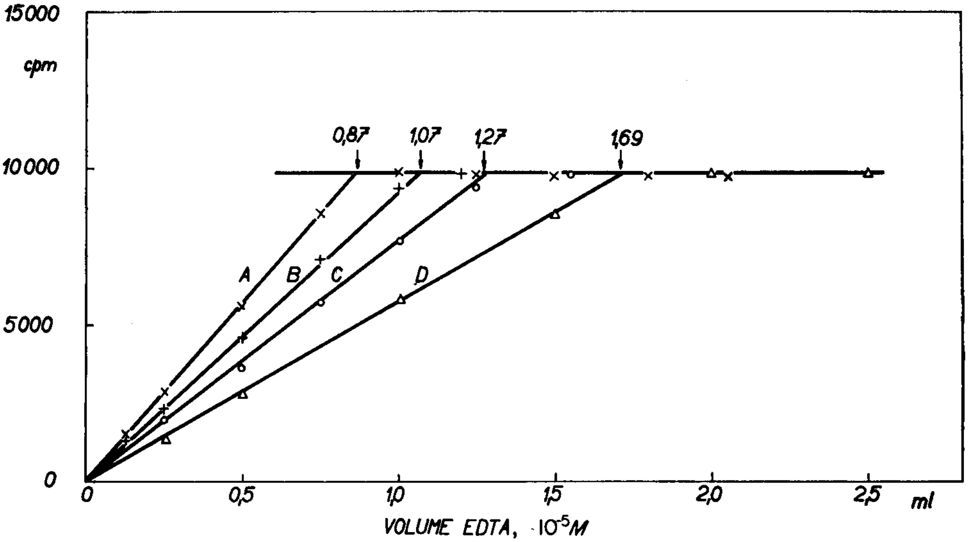


FIG. 1.—Radiometric titration of indium using ^{114}In tracer with $10^{-5}M$ EDTA solution: A—1·00 ml of radio-indium standard solution; B, C, D—1·00, 2·00, 4·00 ml of inactive indium solution mixed with 1·00 ml of radio-indium standard solution.

DETERMINATION OF TRACES OF INDIUM USING ISOTOPIC TRACER

Procedure

The pH of a series of equal, known volumes of analysed solution of indium (2·0 ml containing about 1 μg/ml), labelled with a known amount of radio-indium (^{114m}In, $t_{\frac{1}{2}} = 50$ days), is adjusted approximately to a value of 2–3. Any $iron^{III}$ present, which can interfere, is reduced to $iron^{II}$ by adding 2 drops of 10% ascorbic acid. The solutions thus prepared are carefully mixed with known, increasing amounts of titrating solution ($10^{-5}M$ EDTA) and are simultaneously passed through a series of cation-exchanger columns. The eluate from each column is made up to 10 ml and the activity of 4-ml aliquots are measured by a well-type scintillation counter. Each value of activity measured represents a point on the titration curve (Fig. 1).

The results obtained are also summarised in Table I. The amount of the indium in the non-active sample being analysed can be determined from the difference between the end-point of the standard curve, A (solution containing only standard labelled indium), and the end-points of the corresponding curves, B, C, D (solutions prepared by mixing the standard labelled samples with the sample to be analysed).

TABLE I.—DETERMINATION OF INDIUM

Curve	Indium added, μg	Radio-indium added, μg	Total indium present, μg	Total indium found, μg
A	0·00	1·02	1·02	1·00
B	0·22	1·02	1·24	1·23
C	0·44	1·02	1·46	1·46
D	0·88	1·02	1·90	1·94

DETERMINATION OF TRACES OF COBALT USING NON-ISOTOPIC TRACER

Because of much higher stability with EDTA of the cobalt^{III} complex than of the indium complex it is possible to use radio-indium as non-isotopic tracer for the determination of traces of cobalt.

Procedure

To the series of solutions containing equal, known volumes of the analysed solution (slightly acid), known, increasing amounts of EDTA ($10^{-5}M$) are added. Each of these solutions is carefully mixed in a polyethylene flask with 0·5 ml of 0·01M aqueous ammonia containing 1·5% hydrogen peroxide. The pH of the solutions thus prepared should be 6–8. The solutions are heated on a boiling water bath for 5 min (formation of Co^{III}-EDTA complex). After cooling to room temperature the pH of all the solutions is readjusted to approximately 2–3, and the radio-indium tracer is added. The remainder of the procedure is carried out as before.

The results obtained are given in Fig. 2 and Table II.

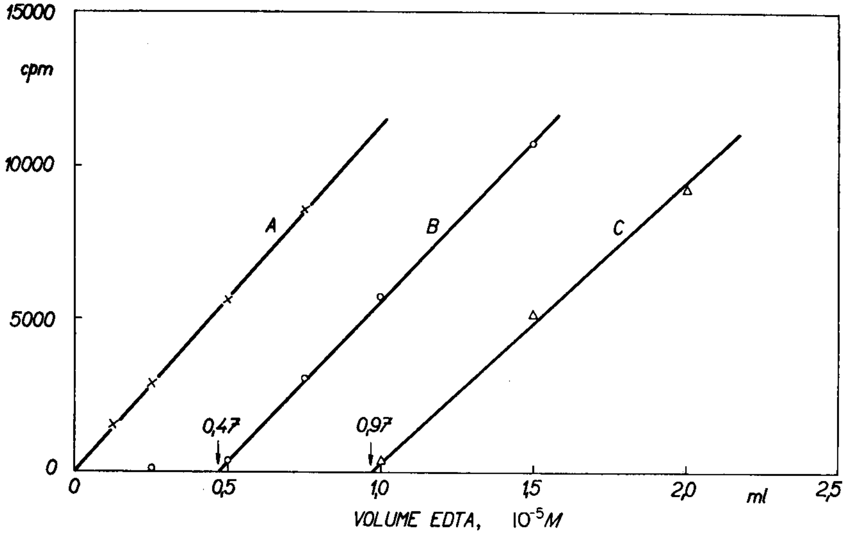


FIG. 2.—Radiometric titration of cobalt using ^{114}In tracer with $10^{-5}M$ EDTA solution: A—1·00 ml of radio-indium standard solution; B, C—1·00, 2·00 ml of inactive cobalt solution.

TABLE II.—DETERMINATION OF COBALT

Curve	Cobalt added, μg	Cobalt found, μg
A	0·00	0·00
B	0·29	0·27
C	0·58	0·56

DISCUSSION

Radiometric titrations such as those described above can in general be used for the same determinations as common complexometric titrations, but their sensitivity is much higher. They have the advantage that the selectivity can be easily predicted from the stability data of EDTA-complexes, which are well known. Thus, for example, in the determination of traces of indium uni- and bivalent metal cations will not interfere, because of their lower stability constants. This has been verified in the present work. However, titrations using isotopic tracers are limited to instances where suitable radioisotopes are available. This restriction does not hold for determinations using non-isotopic tracers. The non-isotopic tracer most suitable for achieving the highest selectivity can also be chosen using the stability constants of the EDTA complexes. The stability constant of the EDTA complex of the tracer must be lower than that of the metal to be determined, but higher than the stability constants of interfering metals which might be present.

Compared with extractive titrations, radiometric titrations using EDTA have the advantage of high stability of the titrant even in very dilute solutions.

Acknowledgement—The authors thank Professor V. Majer, D. Sc. for his interest in this work and to Professor C. L. Wilson for his critical discussion.

Zusammenfassung—Eine neue Art radiometrischer Titration wurde entwickelt. Mit EDTA-Lösungen werden negative oder neutrale Metallchelate gebildet, die leicht mittels Kationenaustauscher von den nicht gebundenen Metallionen abgetrennt werden können. Die Titrationskurven werden aus der Aktivität der Eluate konstruiert. Die Methode wurde an der Bestimmung von Mikrogramm-Mengen Indium mit ^{114m}In als isotopem Tracer und an der Bestimmung von Submikrogramm-Mengen Kobalt mit ^{114m}In als nichtisotopem Tracer verifiziert.

Résumé—On a mis au point un nouveau type de titrage radiométrique. Par l'emploi de solutions d'EDTA, on forme les chélates du métal chargé négativement ou du métal neutre, et ceux-ci peuvent être. aisément séparés des ions en excès qui n'ont pas réagi au moyen d'un échangeur cationique. On trace des courbes de titrage à partir des activités des éluats. On a utilisé la méthode pour doser des quantités d'indium de l'ordre du microgramme par l'emploi de ^{114m}In comme traceur isotopique, ainsi que pour doser des traces de cobalt en quantités inférieures au microgramme au moyen du même indicateur, utilisé comme traceur non isotopique.

REFERENCES

[1] I. P. Alimarin, *Proc. Internat. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, 1956, R/706, 60.

[2] H. Spitzy, *Mikrochim. Acta*, 1960, 789.

[3] J. F. Duncan and F. G. Thomas, *J. Inorg. Nuclear Chem.*, 1957, **4**, 376.

[4] J. Starý and J. Růžička, *Talanta*, 1961, **8**, 775.

[5] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, *Stability Constants, Part* I. The Chemical Society, London, 1957.

Talanta, 1964, Vol. 11, pp. 485 to 493. Pergamon Press Ltd. Printed in Northern Ireland

SOME SULPHUR-CONTAINING ORGANIC COMPOUNDS AS REAGENTS FOR THE PHOTOMETRIC DETERMINATION OF SELENIUM

A. I. BUSEV
Department of Chemistry, M. V. Lomonosov State University
Moscow, U.S.S.R.

(*Received* 29 *July* 1963. *Accepted* 11 *September* 1963)

Summary—The reactions of diethylphosphorodithioate, 2-mercaptobenzimidazole, *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine with selenous acid have been studied. Diethylphosphorodithioate and 2-mercaptobenzimidazole react with selenous acid in a 4:1 molar ratio, and with *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacelyl-*p*-toluidine in a 2:1 ratio. New extraction-photometric methods for the determination of small amounts of selenium in various materials not containing tellurium, have been developed, using 2-mercaptobenzimidazole, *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine as reagents.

THE photometric determination of selenium is carried out mainly in the form of a colloidal solution of elementary selenium or in the form of the piazselenol formed by the reaction of selenous acid with 3,3′-diaminobenzidine.[1,2] No other reagents have found practical application.[3]

Of sulphur-containing reagents it has been reported that selenous acid can react with diethyl phosphorodithioate[4] and with 2-thiopyrogallol,[5] giving yellow compounds which can be extracted with organic solvents. More recent experiments have shown[6,7,8] that many reagents containing sulphydryl groups react with selenous acid, forming yellow compounds which possess sufficient stability to be used for the determination of small amounts of selenium. Some of these reagents possess high sensitivity and selectivity.

In the present work the results are given of a study of the reaction of selenous acid with diethyl phosphorodithioate, 2-mercaptobenzimidazole, and some products of the condensation of thioglycollic acid with primary aromatic amines, together with the photometric methods developed for determining small amounts of selenium in various materials.

Diethyl phosphorodithioate, $(C_2H_5O)_2PSSH$

When an aqueous solution of nickel or potassium diethyl phosphorodithioate, $[(C_2H_5O)_2PSS]_2Ni$ or $(C_2H_5O)_2PSSK$, is added to an aqueous solution of selenous acid at an acidity of between about pH 3 and not greater than 2*M* in hydrochloric acid, a yellowish precipitate is formed. Under these conditions, selenium is quantitatively precipitated by an excess of the reagent. The compound formed consists of needle-shaped, bright yellow crystals with a melting point of 81–82°.[6] Chemical analysis (Se: 17·4%; P:13·6%; S:30·9%) shows that the compound corresponds to the formula $[(C_2H_5O)_2PSS]_2Se$. Therefore selenous acid appears to react with nickel diethyl phosphorodithioate according to the equation:

$$2[(C_2H_5O)_2PSS]_2Ni + H_2SeO_3 + 4HCl \rightarrow [(C_2H_5O)_2PSS]_2Se + [(C_2H_5O)_2PSS]_2 + 2NiCl_2 + 3H_2O.$$

The diethyl phosphorodithioate salt of bivalent selenium is completely stable. In the dry state it can be kept in diffuse daylight for not less than 4 months without visible changes. Its solutions in chloroform have been kept without change for 1 year. Unfortunately, nickel diethyl phosphorodithioate cannot be used to determine selenium either by the gravimetric method (the precipitation takes place slowly) or by the photometric method {the disulphide $[(C_2H_5O)_2PSS]_2$ formed strongly interferes with the photometric determination of the selenium (Fig. 1)}, although the reagent is quite sensitive: the molar absorption coefficient of extracts of the diethyl phosphorodithioate salt of bivalent selenium is 1900.

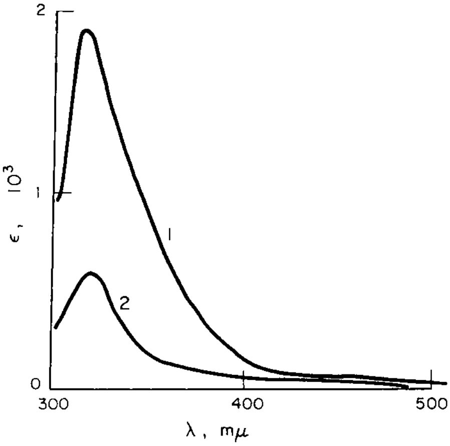
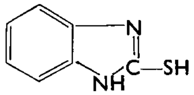


FIG. 1—Absorption curves of the diethyl phosphorodithioate salt of bivalent selenium (1) and the disulphide $[(C_2H_5O)_2PSS]_2$ (2).

2-Mercaptobenzimidazole,



2-Mercaptobenzimidazole has been used for the gravimetric determination of bismuth, copper, cadmium, lead, mercury and gold.[9] Experiments have now shown that 2-mercaptobenzimidazole permits the photometric determination of small amounts of selenium. When a 1 % ethanolic solution of 2-mercaptobenzimidazole is added to an acid solution [the optimum optical density is found at an acidity of from 1 to 3*M* hydrochloric acid (Fig. 2)] of selenous acid, it gives a yellow coloration or a bright yellow crystalline precipitate, depending on its concentration. The compound formed is not extracted by benzene, toluene or ether, is poorly extracted by isoamyl and isobutyl alcohols, is somewhat better extracted by dichloroethane and chloroform, and is well extracted by a 1:5 mixture of butyl alcohol and chloroform, the coloration being very stable. It does not change during several months. The extraction takes place practically completely in a single treatment.

It has not been possible to isolate in the pure state and analyse the compound formed by the reaction of selenous acid with 2-mercaptobenzimidazole, because when it is filtered on paper it decomposes after some minutes with the liberation of red elementary selenium.

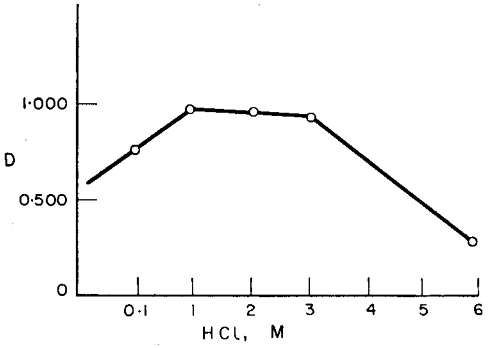


FIG. 2.—Absorption at 335 mμ of the compound of selenium with 2-mercaptobenzimidazole as a function of the acidity of the solution.

The extracts of the compound of 2-mercaptobenzimidazole with selenous acid in a 1:5 mixture of butyl alcohol and chloroform have a maximum light absorption at 330 mμ. The optical density was measured relative to the pure extractant (Fig. 3). If the optical density is measured relative to an extract of the reagent with a mixture of butyl alcohol and chloroform, the maximum light absorption is found at 335 mμ.

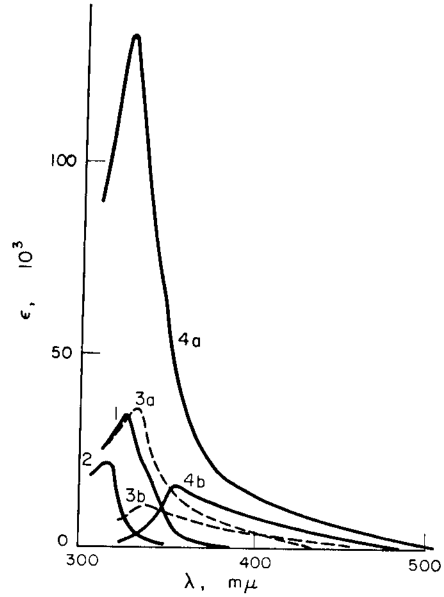


FIG. 3.—Absorption curves of 2-mercaptobenzimidazole (1), $(C_7H_5N_2S)_2$ (2), and the compounds of 2-mercaptobenzimidazole with selenium (3a, 3b) and with tellurium (4a, 4b) relative to the pure extractant (3a, 4a) and relative to an extract of the reagent (3b, 4b).

Under the experimental conditions, the reagent is itself extracted to a large extent and it absorbs light intensely; its maximum absorption is at 325 mμ (Fig. 3). The molar absorption coefficient of extracts of the compound of selenium with 2-mercaptobenzimidazole was found to be 10,500.

The method of isomolar series has shown that selenous acid reacts with 2- mercaptobenzimidazole in a molar ratio of 1:4. This suggests that the reaction between selenous acid and 2-mercaptobenzimidazole takes place according to the equation:

$$4C_7H_6N_2S + H_2SeO_3 \rightarrow (C_7H_5N_2S)_2Se + (C_7H_5N_2S)_2 + 3H_2O.$$

Extracts of the compound of selenium with 2-mercaptobenzimidazole obey Beer's law within the range of concentrations from 1 to 10 μg/ml at 360–380 mμ and 1–40 μg/ml at 420 mμ (Fig. 4). Satisfactory results for the determination of selenium are obtained by measuring the optical density of extracts of its compound with 2-mercaptobenzimidazole in the region of wavelengths greater than 360 mμ or, best, at 420 mμ. At wavelengths less than 360 mμ, the reagent itself absorbs light and thereby prevents satisfactory results being obtained.

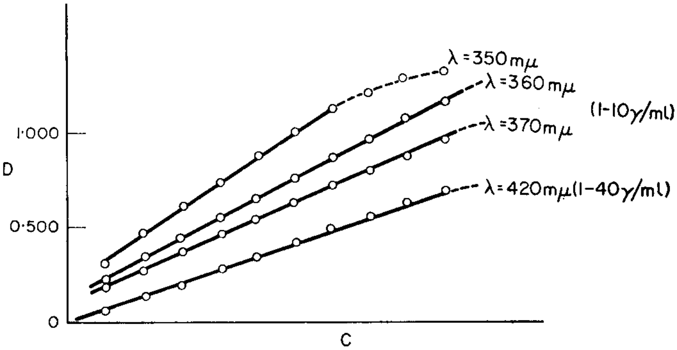
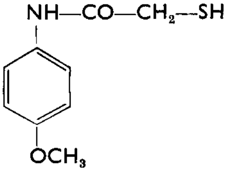


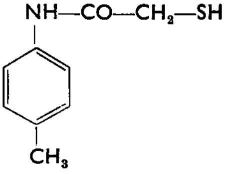
FIG. 4.—Obedience to Beer's law of the compound of selenium with 2-mercaptobenzimidazole at various wavelengths.

Derivatives of thioglycollic acid

A series of derivatives of thioglycollic acid, RNH-CO-CH_2-SH, (where R is -$C_6H_4OCH_3$-*p*, -$C_6H_4CH_3$-*p*, -C_6H_4Cl-*m*, -$C_6H_4NO_2$-*m*, *etc.*) has been used for the detection and gravimetric and photometric determination of silver, lead, mercury^{I}, mercury^{II}, copper, cadmium, bismuth, tin, zinc, cobalt, nickel and molybdenum.[10,11] Experiments have now shown that some of these derivatives can be used for the photometric determination of small amounts of selenium. As examples, the results are given of a study of two derivatives of thioglycollic acid obtained by the condensation of the latter with *p*-anisidine and *p*-toluidine, respectively:



N-mercaptoacetyl-*p*-anisidine



N-mercaptoacetyl-*p*-toluidine

When a solution of selenous acid is added to an acid solution of either of these reagents [the optimum optical density is found at an acidity of 0·05–1M hydrochloric acid in the case of *N*-mercaptoacetyl-*p*-anisidine and 0·05–0·5M hydrochloric acid in the case of *N*-mercaptoacetyl-*p*-toluidine (Fig. 5)], a yellow coloration or pale yellow turbidity or precipitate is immediately formed which can be extracted with many organic solvents: benzene, chloroform, *etc.* The extracts are yellow and are very stable. The extraction of selenium in the form of the coloured compounds takes place practically completely in a single extraction with a 1:5 mixture of butyl alcohol and chloroform.

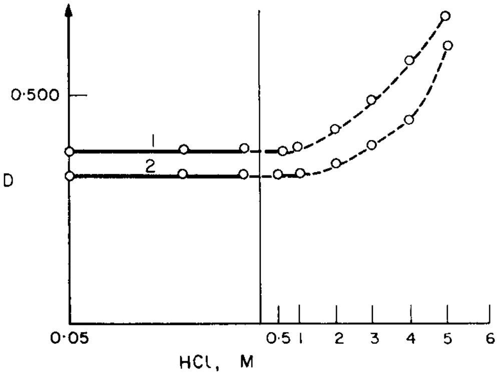


FIG. 5.—Absorption of the compounds of selenium with *N*-mercaptoacetyl-*p*-anisidine (1) and *N*-mercaptoacetyl-*p*-toluidine (2) as a function of the acidity of the solution.

The absorption curves of the extracts of the compound of selenium with *N*-mercaptoacetyl-*p*-anisidine have a maximum at 310 mμ relative to the pure extractant and at 315 mμ relative to an extract of the reagent (Fig. 6). The extract of the reagent itself under the experimental conditions also absorbs light intensely; its absorption curve has a maximum at 306 mμ (Fig. 6).

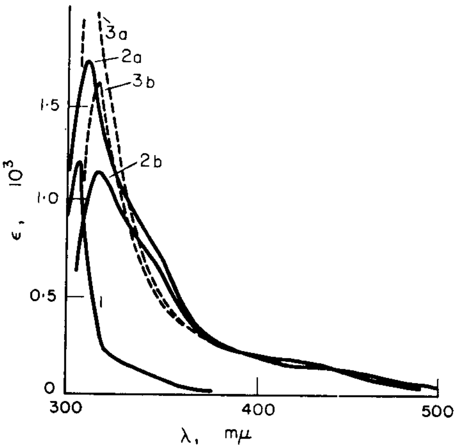


FIG. 6.—Absorption curves of *N*-mercaptoacetyl-*p*-anisidine (1) and its compounds with selenium (2a, 2b) and with tellurium (3a, 3b) relative to the pure extractant (2a, 3a) and to an extract of the reagent (2b, 3b).

N-Mercaptoacetyl-*p*-toluidine is also extracted well under the experimental conditions, but its extract absorbs light very feebly and therefore all the absorption curves of extracts of the compound of selenium with *N*-mercaptoacetyl-*p*-toluidine relative to the pure extractant and relative to an extract of the reagent have maxima in the same position at 318 mμ (Fig. 7). The molar absorption coefficients of the compounds of selenium with *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine are similar at 1200.

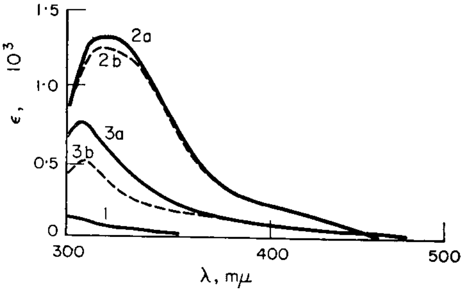


FIG. 7.—Absorption curves of *N*-mercaptoacetyl-*p*-toluidine (1) and its compounds with selenium (2a, 2b) and with tellurium (3a, 3b) relative to the pure extractant (2a, 3a) and to an extractant of the reagent (2b, 3b,).

The molar ratio in which selenous acid reacts with these reagents was found to be 1:2 (Fig. 8). Thus selenous acid probably reacts according to the following equations:

$$2C_9H_{11}O_2NS + H_2SeO_3 \rightarrow (C_9H_{10}O_2NS)_2SeO + 2H_2O$$
$$2C_9H_{11}ONS + H_2SeO_3 \rightarrow (C_9H_{10}ONS)_2SeO + 2H_2O.$$

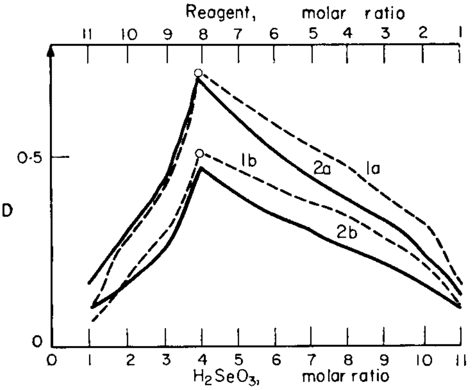


FIG. 8.—Determination of the molar ratios in the reaction of selenous acid with *N*-mercaptoacetyl-*p*-anisidine (1a, 1b) and *N*-mercaptoacetyl-*p*-toluidine (2a, 2b) at 340 mμ (1a, 2a) and 360 mμ (1b, 2b).

It has not been possible to isolate in the pure state and analyse the selenium compounds formed because they are unstable. After they have been filtered, red selenium appears on the filter after a few minutes.

Extracts of the compounds of selenium with *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine obey Beer's law within the range of concentrations from 8 to 70 μg/ml at wavelengths from 340 mμ to 380 mμ. At wavelengths greater than

380 mμ, the extracts still follow Beer's law, but the sensitivity is considerably less. At wavelengths less than 340 mμ, *N*-mercaptoacetyl-*p*-anisidine itself absorbs light and thereby prevents satisfactory results being obtained. In the case of *N*-mercaptoacetyl-*p*-toluidine, the lower limit of obedience of the extracts to Beer's law can be reduced to concentrations below 7 μg/ml, but it is then necessary to work with a hydrogen lamp.

It must be mentioned that 2-mercaptobenzimidazole, *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine permit the determination of selenium only in the absence of tellurium. Tellurous acid, as can be seen from Figs. 3, 6 and 7, behaves completely analogously to selenous acid under the experimental conditions. It reacts with the reagents mentioned, likewise forming either a yellow coloration or a precipitate. The tellurium compounds formed are also extracted by organic solvents. The light-absorption maxima of the extracts of the tellurium compounds and the corresponding selenium compounds are very close to one another (Table I). Consequently, in order to determine selenium in materials containing tellurium, the latter must previously be removed.

TABLE I.—ABSORPTION MAXIMA OF COMPOUNDS OF SELENIUM AND TELLURIUM WITH VARIOUS REAGENTS

Reagent	λ_m(Se)	λ_m(Te)
2-Mercaptobenzimidazole	335	350
N-Mercaptoacetyl-*p*-anisidine	315	325
N-Mercaptoacetyl-*p*-toluidine	318	308

Bismuth and copper interfere with the determination of selenium by the proposed reagents, with which they form either greyish-yellow or pale yellow precipitates which are partially extractable with organic solvents, giving yellow extracts. Moderate amounts of mercury, silver, gold, cadmium and lead cause practically no interference. Bromate and iodate interfere with the determination of selenium with 2-mercaptobenzimidazole, and molybdate interferes with its determination by means of *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine.

Determination of selenium in various materials not containing tellurium

A 0·1 to 0·5-g sample of the material to be analysed is dissolved by means of a mixture of nitric, hydrochloric and sulphuric acids.[12] Any excess of nitrous acid is removed by the addition of urea.[13] The resulting solution is diluted with twice its volume of distilled water and any insoluble residue is filtered off through a loose filter. The filtrate is diluted in volumetric flasks with appropriate volumes of water to give concentrations of selenium in the resulting solution within the range 50 to 200 μg/ml.

One-five ml of the solution to be analysed is added by means of a pipette to an acid solution of the reagents namely 3 ml 1% ethanolic solution of 2-mercaptobenzimidazole, or 3 ml 0·2% ethanolic solution of *N*-mercaptoacetyl-*p*-anisidide or *N*-mercaptoacetyl-*p*-toluidine (final concentration 2*M* hydrochloric acid in the case of 2-mercaptobenzimidazole and 0·5*M* hydrochloric acid in the case of *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine) in a separating funnel and the mixture is well shaken, then extracted with 5 ml of a 1:5 mixture of butyl alcohol and chloroform. It is left to stand for 1 hr for complete separation of the aqueous and organic phases. The extracts are filtered through a dry filter paper into 10·00-mm cells and the optical density measured on a spectrophotometer Beckman DU at the appropriate wavelength (420 mμ for 2-mercaptobenzimidazole and 360 mμ for *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine). The selenium content is found from a calibration curve.

Calibration curves are obtained as above, using different amounts of a standardised solution of selenous acid. The completion of a single selenium determination requires 4 hr.

Some results for the determination of selenium are given in Tables II, III and IV.

TABLE II.—DETERMINATION OF SELENIUM IN A PURE COMPOUND BY MEANS OF 2-MERCAPTOBENZIMIDAZOLE

SeO_2 taken, *mg*	Se found, *mg*	Error, %
100·0	72·0	+1·5
50·0	36·3	+2·6
10·0	7·3	+2·6
2·0	1·5	+5·4

TABLE III.—DETERMINATION OF SELENIUM IN MATERIALS NOT CONTAINING TELLURIUM BY MEANS OF 2-MERCAPTOBENZIMIDAZOLE

Material to be analysed	Weight of sample, *g*	Composition, %	Se found, %	Absolute error, %
Dust from a sintering plant	0·500	Se 0·51; Tl 0·11; Ge 0·0011; In 0·0009;	0·54	+0·03
Sinter	0·100	4·42; remainder unknown	4·57	+0·15
Se-Hg sludge	0·100	Se 14·6; Hg 9·5; remainder $PbSO_4$	14·2	−0·4
Sublimate from Se-As filter-cake	0·100	Se 30·0; As about 20; Pb present	31·25	+1·25

TABLE IV.—DETERMINATION OF SELENIUM IN MATERIALS NOT CONTAINING TELLURIUM BY MEANS OF *N*-MERCAPTOACETYL-*p*-ANISIDINE AND *N*-MERCAPTOACETYL-*p*-TOLUIDINE

Material to be analysed	Composition, %	Se found, %			
		With *N*-mercapto acetyl-*p*-anisidine	Absolute error, %	With *N*-mercapto acetyl-*p*-toluidine	Absolute error, %
Dust from a sintering plant	Se 0·51; Tl 0·11; Ge 0·0011; In 0·0009	0·49	−0·02	0·46	−0·05
Sinter	Se 4·42; remainder unknown	4·60	+0·18	4·11	−0·31
Se-Hg sludge	Se 14·6; Hg 9·5; remainder $PbSO_4$	14·85	+0·25	14·37	−0·23
Sinter	Se 0·03; remainder unknown	0·028	−0·002	0·026	−0·004

Acknowledgement—Hoang Minn-Chau took part in the experimental work.

Zusammenfassung—Die Reaktion von Diäthylphosphorodithioat, 2-Mercaptobenzimidazol, N-Mercaptoacetyl-*p*-anisidin und N-Mercaptoacetyl-p-toluidin mit seleniger Säure wurden untersucht. Die ersten zwei Verbindungen reagieren mit seleniger Säure im Verhältnis 4:1, die andern beiden im Verhältnis 2:1. Neue extraktionsphotometrische Methoden zur Bestimmung kleiner Selenmengen in verschiedenen nicht tellurhaltigen Materialien wurden entwickelt mit 2-Mercaptobenzimidazol, N-Mercaptoacetyl-p-anisidin und N-Mercaptoacetyl-p-toluidin als Reagentien.

Résumé—On a étudié des réactions du diéthylphosphorodithioate, de la mercapt-2-benzimidazole, de la N-mercaptoacétyl-p-anisidine et de la N-mercaptoacétyl-p-toluidine, avec l'acide sélénieux. Le diéthylphosphorodithioate et la mercapto-2-benzimodazole réagissent avec l'acide sélénieux dans le rapport moléculaire de 4/1. La N-mercaptoacétyl-p-anisidine et la N-mercapto-p-toluidine réagissent dans le rapport 2/1. Etude de nouvelles méthodes photométriques d'extraction pour le dosage de petites quantités de sélénium dans des produits variés et ne contenant pas de tellure; on utilise la mercapto-2-benzimidazole, la N-mercaptoacétyl-p-anisidine et la N-mercaptoacétyl-p-toluidine comme réactifs.

REFERENCES

[1] J. Hoste and J. Gillis, *Analyt. Chim. Acta*, 1955, **12**, 158.
[2] K. L. Cheng, *Analyt. Chem.*, 1956, **28**, 1738.
[3] D. F. Boltz, *Colorimetric Determination of Nonmetals.* Interscience Publishers Inc., New York, 1958, p. 309.
[4] A. I. Busev and M. I. Ivanyutin, *Trudy Kom. analit. Khim., Akad. Nauk. S.S.S.R.*, 1960,**11**, 172.
[5] V. M. Dziomko and A. I. Cherepakin, *Sbornik Stateĭ Vses. Zaoch. Politekh. Inst.*, 1955 (9), 65.
[6] A. I. Busev and Hoang Minn-Chau, *Zhur. neorg. Khim.*, 1962, **7**, 88.
[7] *Idem, Zhur. analit. Khim.*, 1962, **17**, 1091.
[8] *Idem, ibid.*, 1963, **18**, 360.
[9] F. J. Welcher, *Organic Analytical Reagents*, Vol IV. Van Nostrand, New York, 1948, p. 127.
[10] R. N. Misra and S. S. Guha Sircar, *J. Indian Chem. Soc.*, 1955, **32**, 127.
[11] R. S. Swain, R. N. Misra and S. S. Guha Sircar, *ibid.*, 1956, **33**, 329.
[12] A. A. Kudryavtsev, *Chemistry and Technology of Selenium and Tellurium.* Goskhimizdat "Vysshaya shkola", Moscow, 1961, p. 214.
[13] E. S. Gould, *Analyt. Chem.*, 1951, **23**, 1502.

Talanta, 1964, Vol. 11, pp. 495 to 500. Pergamon Press Ltd. Printed in Northern Ireland

ANION-EXCHANGE BEHAVIOUR OF SCANDIUM IN CHLORIDE-THIOCYANATE MEDIA

HIROSHI HAMAGUCHI, NAOKI ONUMA, MASANORI KISHI and ROKURO KURODA
Department of Chemistry, Tokyo Kyoiku University, Koishikawa, Tokyo, Japan

(*Received* 29 *July* 1963. *Accepted* 22 *October* 1963)

Summary—A method is described for the separation of scandium from rare earths and thorium by anion exchange. The method utilises the adsorption of a negatively-charged thiocyanato complex of scandium on the strongly-basic anion exchanger Dowex 1-X8 from a 2*M* solution of ammonium thiocyanate in 0·5*M* hydrochloric acid. Rare earth elements are not retained on the column, while scandium and thorium show moderate adsorptions and can be separated chromatographically by elution with 3*M* hydrochloric acid. The distribution coefficient data for elements in this medium suggest many possible analytical separations of scandium.

MOST ion-exchange separations of scandium have been based on the use of cation exchangers with eluents containing an organic complexing agent. Thus, elution with citric acid,[1] nitrilotriacetic acid,[2] ethylenediaminetetra-acetic acid,[2] hydrazine diacetic acid[3] and ammonium acetate-ammonium oxalate solution[4] seem to provide an excellent cation-exchange separation of scandium from rare earth elements. There has been little published information about the effective anion-exchange separation of scandium from rare earths and thorium. Vickery[5] has demonstrated that scandium in citrate or oxalate solution is adsorbed on an anion-exchange resin. Scandium is also weakly adsorbed from 13·3*M* hydrochloric acid, which affords the basis of a simple separation from rare earths,[6] but thorium also behaves like scandium. Walter[7] has effected the separation of scandium, titanium and vanadium by anion exchange from oxalic-hydrochloric acid mixtures and Schindewolf and Irvine[8] worked out the separation of traces of scandium from the same elements by anion exchange from 0·5 to 15*M* hydrofluoric acid solution. The adsorption of several metals, including scandium, on Dowex-1 from potassium thiocyanate solution has been reported by Turner, Philp and Day,[9] the separation of scandium and chromium having been accomplished. In a recently published study Fritz and Pietrzyk[10] have reported distribution coefficients for dysprosium, lanthanum and scandium in mixtures of hydrochloric acid and several alcohols. Yttrium and scandium were separated from lanthanum in hydrochloric acid-ethanol mixtures by Wilkins and Smith,[11] while Faris and Warton[12] worked out an extensive spectrographic determination of distribution coefficients for scandium, yttrium and rare earths in nitric acid-methanol mixtures, giving a promising separation factor for scandium from rare earths.

A study of the anion-exchange behaviour of scandium in an ammonium thiocyanate-hydrochloric acid system was, therefore, undertaken to provide information which would give a method for the sharp separation of scandium from the whole of the lanthanide elements and thorium as well as from several common metals.

EXPERIMENTAL

Ion-exchange resin

Dowex 1-X8, 100–200 mesh, was used in the thiocyanate form. Before use the resin was placed in a large column and back-washed with distilled water to remove fine particles. It was then washed with 3*M* hydrochloric acid, followed by a sufficient amount of 3*M* ammonium thiocyanate solution to convert it to the thiocyanate form. After washing with distilled water the resin was dried at 50° for 1 hr, then placed in a large desiccator containing saturated potassium bromide solution.

Resin column

Ten g of dried resin were slurried with distilled water and poured into a conventional ion-exchange column, 1·1 cm in diameter, packed at the bottom with glass wool. The column bed usually had a height of approximately 18 cm. Eluent was added dropwise from a conventional separatory funnel attached to the top of the column through a rubber stopper.

Reagents and tracer

Scandium^{III} solution (0·600 mg of scandium/ml) was made by dissolving *ca.* 100 mg of 99·9% purity Sc_2O_3 in 3*M* hydrochloric acid, evaporating to dryness and diluting to 100 ml with 0·5*M* hydrochloric acid. Lanthanum and lutetium chloride solutions (2·85 mg of lanthanum/ml; 1.83 mg of lutetium/ml) were prepared by dissolving the appropriate amount of the respective oxide (99·9% purity) in 3*M* hydrochloric acid, evaporating to dryness and diluting to a definite volume with 0·5*M* hydrochloric acid. Thorium chloride solution (4·85 mg of thorium/ml) was made by simply dissolving *ca.* 820 mg of thorium chloride in 100 ml of 0·5*M* hydrochloric acid.

The strengths of the above solutions were determined by titration with 0·001*M* EDTA solution previously standardised against primary-standard zinc metal. All other reagents used were of analytical-reagent quality.

^{46}Sc (half-life 85 day) and ^{160}Tb (73 day) tracers were produced by irradiating 40 mg of the appropriate oxide in the Japan Research Reactor JRR-1 for 15 hr at a power level of 50 kW and a neutron flux of 3×10^{11} neutron.cm^{-2}.sec^{-1}. After cooling for a sufficient period of time each oxide was dissolved in hydrochloric acid, evaporated to dryness and the residue taken up in 0·5*M* hydrochloric acid to give a final volume of 100 ml. An aliquot, usually 0·5 ml for scandium and 1 ml for terbium, was used for elution work. A 0·5*M* hydrochloric acid solution of carrier-free ^{152}Eu (13 year) was obtained commercially. An aliquot was taken, evaporated and diluted to 100 ml of 0·5*M* hydrochloric acid, to give a suitable level of activity. Each tracer was carefully checked for radiochemical purity before use by gamma spectrometry.

Column separation of scandium

A sample solution containing scandium and rare earth or thorium is evaporated and taken up in a minimum amount of 2*M* ammonium thiocyanate in 0·5*M* hydrochloric acid. The resin bed should be previously equilibrated with the same solution. Load the sample solution onto the top of the column. When the liquid level in the column has almost reached the top of the resin bed, elution is started with 3*M* hydrochloric acid at room temperature. The rate of flow of eluent through the column is adjusted to be approximately 0·17 ml/min and the effluent is collected in 5- or 10-ml fractions. These fractions are transferred to a beaker, diluted with water and titrated with 0·001*M* EDTA using Xylenol Orange as indicator. In the cases of separation of europium or terbium from scandium a quantitative measure of their concentration in the effluent fractions is obtained by counting the respective total gamma activity using a standard well-type scintillation counter.

RESULTS AND DISCUSSION

Like hydrochloric acid, thiocyanic acid (a pseudohalogenic acid), forms stable thiocyanato complexes with a number of metals and it has been put to analytical use in connection with solvent extraction using diethyl ether. Some attention[9,13,14,15,16] has been paid to the use of thiocyanate with or without hydrochloric acid in ion-exchange separations. Korkisch and Hecht[16] devised a separation of gallium, iron and aluminium, by the use of a thiocyanate elution system. In a weakly acid solution gallium and iron form negatively-charged thiocyanato complexes which are adsorbed on an anion-exchange column, while aluminium passes through the column with no sign of adsorption. Gallium and iron are then chromatographically desorbed by elution with hydrochloric acid which decreases the stability of the respective thiocyanato complexes.

It is of interest to note here that the elution system enhances the tendency of scandium and thorium to behave as anionic species; from a hydrochloric acid medium both elements do not show any marked adsorption on an anion-exchange resin.

Fig. 1 illustrates the quantitative elution profile curves when scandium and rare

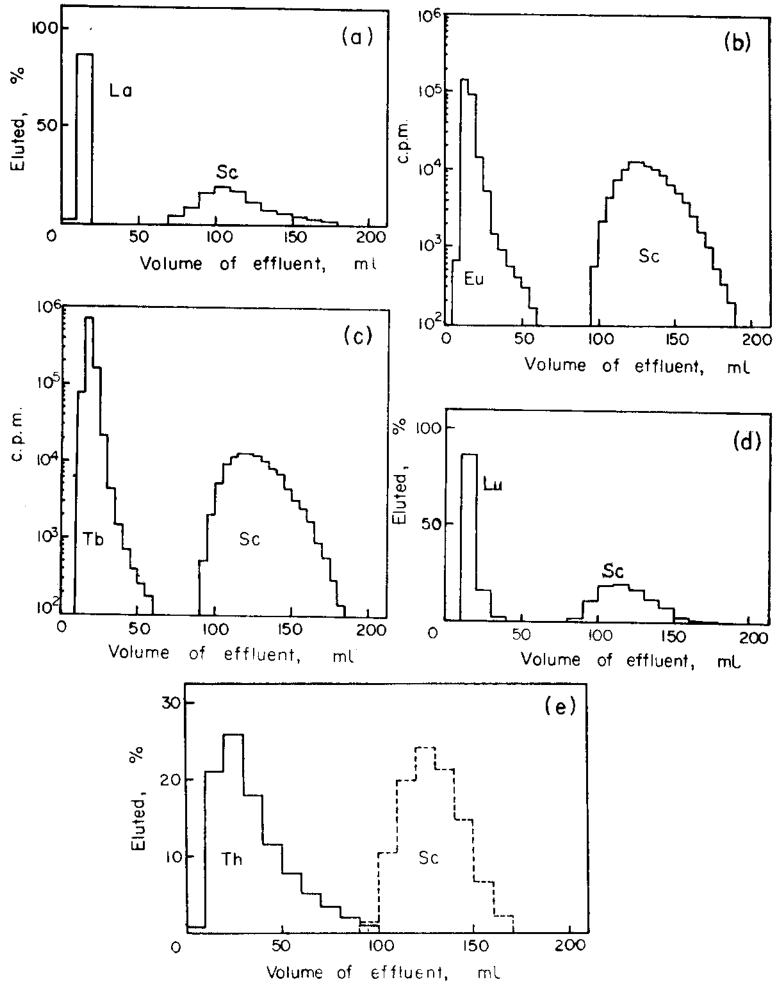


FIG. 1.—Elution profile curves

(*a*) The elution with $3M$ HCl of La and Sc from an 18 × 1·1 cm column of Dowex 1 X8, 100–200 mesh, previously treated with $2M$ NH_4SCN in $0{\cdot}5M$ HCl. La 2·9 mg, Sc 0·6 mg present with recovery of 98% for La and 99% for Sc.

(*b*) The elution with $3M$ HCl of ^{152}Eu and ^{46}Sc from the same column as in (*a*). Eu carrier-free, Sc 130 μg present with recovery of 87% for Eu and 98% for Sc.

(*c*) The elution with $3M$ HCl of ^{160}Tb and ^{46}Sc from the same column as in (*a*). Tb 350 μg, Sc 130 μg present with recovery of 99% for Tb and 99% for Sc.

(*d*) The elution with $3M$ HCl of Lu and Sc from the same column as in (*a*). Lu 1·8 mg, Sc 0·6 mg present with recovery of 100% for Lu and 98% for Sc.

(*e*) The elution with $3M$ HCl of Th and Sc from the same column as in (*a*). Th 4·9 mg, Sc 0·6 mg present.

TABLE I.—DISTRIBUTION COEFFICIENT OF SOME ELEMENTS IN NH_4SCN-HCl MEDIUM ON DOWEX 1-X8

Element	Concentration of NH_4SCN in 0·5*M* HCl, *M*				
	0·2	0·4	0·6	0·8	1·0
Sc	56	250	905	5040	2818
La	<1	<1	<1	<1	<1
Sm	<1	<1	<1	<1	<1
Lu	<1	<1	<1	<1	<1
Th	3·3	19	43	74	106
Ca	0·0	0·0	0·0	0·0	0·0
Al	0·0	0·0	0·7	0·7	0·9
Cu	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Zn	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Cd	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
In	579	646	734	580	706
Hg	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$

Kd value of Sc in 2*M* NH_4SCN—0·5*M* HCl is $>10^4$.

TABLE II.—SEPARATION OF SCANDIUM FROM OTHER ELEMENTS IN NH_4SCN-HCl MEDIUM

Scandium μg		Foreign ions used, *mg*		Foreign ions		Remark
Taken	Found			Break-through	Elution complete	
600	598	Al	3·4	0	60	Al eluted first, then Sc with 3*M* HCl.
600	599	Ca	2·0	0	60	Ca eluted first, then Sc with 3*M* HCl.
600	601	Fe	1·0	—	—	Sc eluted first with 3*M* HCl; Fe strongly adsorbed on resin.
600	592	Zn	1·3	210	300	Sc eluted first with 3*M* HCl, then Zn with H_2O.
600	588	Cd	1·1	210	300	Sc eluted first with 3*M* HCl, then Cd with H_2O.
600	594	In	1·8	210	270	Sc eluted first with 3*M* HCl, then In with 0·005*M* HCl.
600	592	La	2·9	0	20	La eluted first, then Sc with 3*M* HCl.
600	588	Lu	1·8	10	40	Lu eluted first, then Sc with 3*M* HCl.

earth or thorium are eluted by 3*M* hydrochloric acid. It can be seen that scandium can be separated successfully from lanthanum, europium, terbium and lutetium. Scandium tends to give slightly asymmetrically-shaped elution bands. This would result either from rather slow approach to exchange equilibrium or from non-linearity of the adsorption isotherm. According to an equilibrium study by a batch method it takes more than 20 hr for scandium to attain exchange equilibrium in the anion exchanger-thiocyanic acid system at room temperature.

In cation-exchange chromatography with elution by hydrochloric acid-ammonium thiocyanate, heavy rare earth elements ranging from europium to lutetium can be separated from scandium with difficulty.[14] Extreme difficulty has been encountered in separating scandium from heavier rare earths, even in lactate, citrate and EDTA eluent systems coupled with a cation exchanger. Scandium is eluted between thulium and erbium in close proximity to thulium in the form of a complex with EDTA by anion-exchange chromatography.[17] The anion-exchange separation of scandium presented here is likely to offer a simple, rapid and convenient way to separate scandium successfully with a rather shorter column.

The separation of thorium is not very satisfactory, but it may be achieved by the use of a slightly longer column or, more effectively, by the proper choice of eluent system, say 0·2*M* ammonium thiocyanate in 0·5*M* hydrochloric acid. In this case it is preferable to desorb scandium with hydrochloric acid after elution of the thorium fraction in order to minimise the tailing of scandium elution.

In Table I the weight distribution coefficient values, Kd, are given for several elements.

Increasing the concentration of thiocyanate resulted in an increased adsorption of scandium and thorium. The adsorption of scandium was found to be almost independent of the concentration of hydrochloric acid over the range 0·25*M* to 2·0*M*. The feasibility of the separation of scandium from common metal ions was investigated briefly. In Table II several of the results obtained are recorded. Scandium is completely eluted by a 130 ml-fraction of 3*M* hydrochloric acid, while the breakthrough of aluminium and calcium occurred in the effluent from the sample solution. Because iron, copper, indium and mercury are not desorbed with 3*M* hydrochloric acid, the separation of scandium from most metal ions which form strong thiocyanato complexes should be feasible.

Zusammenfassung—Eine Methode zur Trennung von Scandium von seltenen Erden und Thorium durch Anionenaustausch wird beschrieben. Dabei wird der negativ geladene Rhodanokomplex von Scandium am stark basischen Anionenaustauscher Dowex 1-X8 aus einer Lösung mit 2m NH_4SCN und 0,5m HCl adsorbiert. Seltene Erden werden auf der Säule nicht zurückgehalten, Scandium und Thorium werden mäßig stark adsorbiert und können chromatographisch durch Elution mit 3m HCl getrennt werden. Die Verteilungskoeffizienten für verschiedene Elemente in diesem Medium weisen auf viele mögliche analytische Abtrennungsverfahren für Scandium hin.

Résumé—On décrit une méthode de séparation du scandium des terres rares et du thorium par échange d'anions. La méthode utilise l'adsorption, sur l'échangeur anionique fortement basique Dowex 1-X8, d'un complexe sulfocyané du scandium chargé négativement, à partir d'une solution 2*M* de sulfocyanure d'ammonium en acide chlorhydrique 0,5*M*. Les éléments des terres rares ne sont pas retenus sur la colonne, cependant que le scandium et le thorium sont moyennement adsorbés et peuvent être séparés chromatographiquement par élution à l'acide chlorhydrique 3M. Les données sur les coefficients de distribution des éléments dans ce milieu suggèrent de nombreuses séparations analytiques possibles du scandium.

REFERENCES

[1] P. Radhakrishna, *Analyt. Chim. Acta*, 1953, **8**, 140.
[2] K. Iya and J. Loviers, *Compt. rend.*, 1953, **237**, 1413; R. C. Vickery, *J. Chem. Soc.*, 1955, 245.
[3] R. C. Vickery, *The Chemistry of Yttrium and Scandium.* Pergamon Press Ltd., Oxford, 1960, p. 75.
[4] H. Hamaguchi, R. Kuroda, R. Sugisita, N. Onuma and T. Shimizu, *Analyt. Chim. Acta*, 1963, **28**, 61.
[5] R. C. Vickery, *J. Chem. Soc.*, 1955, 245.
[6] J. Yoshimura, Y. Takashima and H. Waki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79**, 1169.
[7] R. I. Walter, *J. Inorg. Nuclear Chem.*, 1958, **6**, 58.
[8] U. Schindewolf and J. W. Irvine, Jr., *Analyt. Chem.*, 1958, **30**, 906.

[9] J. B. Turner, R. H. Philp and R. A. Day, Jr., *Analyt. Chim. Acta*, 1962, **26**, 94.
[10] J. S. Fritz and D. J. Pietrzyk, *Talanta*, 1961, **8**, 143.
[11] D. H. Wilkins and G. E. Smith, *ibid.*, 1961, **8**, 138.
[12] J. P. Faris and J. W. Warton, *Analyt. Chem.*, 1962, **34**, 1077.
[13] H. Hamaguchi, R. Kuroda and N. Onuma, *Talanta*, 1963, **10**, 120.
[14] H. Hamaguchi, R. Kuroda, K. Aoki, R. Sugisita and N. Onuma, *ibid.*, 1963, **10**, 153.
[15] J. P. Surls, Jr. and G. R. Choppin, *J. Inorg. Nuclear Chem.*, 1957, **4**, 62.
[16] J. Korkisch and F. Hecht, *Microchim. Acta*, 1956, 1230.
[17] J. Minczewski and R. Dybczyński, *J. Chromatog.*, 1962, **7**, 568.

Talanta, 1964, Vol. 11, pp. 501 to 506. Pergamon Press Ltd. Printed in Northern Ireland

EINE PHOTOMETRISCHE METHODE ZUR BESTIMMUNG GERINGER MENGEN VON GOLD MIT *N,N'*-TETRAMETHYL-*o*-TOLYDIN (TETRON)

CH. DAIEV und N. JORDANOV
Chemische Fakultät der Universität zu Sofia, und
Institut für allgemeine und anorganische Chemie an der Bulgarischen Akademie
der Wissenschaften in Sofia

(*Eingegangen am* 29 *Juli* 1963. *Angenommen am* 13 *September* 1963)

Zusammenfassung—Anhand einer Möglichkeit, die vorher grundsätzlich aufgeklärt war, wurde eine photometrische Methode zur Bestimmung geringer Goldmengen mit *N,N'*-Tetramethyl-*o*-tolydin (Tetron) entwickelt. Das Gold wurde von den Begleitelementen zunächst durch Mitfällung mit Tellur, ferner durch Extraktion mit Äther aus Bromwasserstoffsäurem Medium getrennt und schliesslich mit Tetronlösung behandelt. Es entstand eine orangegelbe Färbung, die in etwa 4 Minuten zur vollen Intensität gelangte. Man verdünnte und photometrierte bei Blaulichtfilter. Die Färbung blieb 20 bis 25 Minuten bestehen, verblasste dann allmählich. Das Verfahren wurde zur Bestimmung von Gold in Kupfer-, Blei- und gemischten Konzentraten sowie im Anodenkupfer verwendet. Die Aussagen wurden statistisch ausgewertet.

BEKANNT sind zahlreiche Farbreaktionen für Gold(III)-ionen mit verschiedenen organischen Reagentien.[2–18] Den meisten von ihnen liegen photometrische Methoden zur Bestimmung geringer Goldmengen zugrunde. Eine kritische Bewertung derselben ergibt,[19] dass am empfindlichsten diejenige ist, bei der das o-Tolydin als Reagens verwendet wird.

Unsere Untersuchungen zeigten,[1] dass *N,N'*-Tetramethyl-o-tolydin (Tetron) etwa zweimal so empfindliche Reaktionen bewirkt als das o-Tolydin; auch ist hierbei die Färbung seiner Oxydationsform tiefer und nachhaltiger. Der Extinktionskoeffizient der unter der Einwirkung von Gold(III)-ionen entstandenen Oxydationsform des Tetrons beträgt 50,000 bei Blaulichtfilter des ФЭК–М. Die Geschwindigkeit des Redoxprozesses hängt von der Acidität des Mediums ab. In schwefelsaurem Medium (1:20) kommt die Färbung zur vollen Entwicklung in 3 bis 4 Min., bleibt 20 bis 25 Min. unverändert und verblasst dann allmählich. Direktes Sonnenlicht beschleunigt die Entfärbung, daher sind die Lösungen davor zu schützen.

Dass hierbei Fe(III), Cu, Mn(II), Pb, As, Sb, Sn, Ni, Co, Zn, Ag, Hg, Se, Te und Tl nicht störend wirken, wohl aber Ce(IV), Mn(IV), Ir(IV), Chromat- und Nitritionen, ergibt sich eindeutig aus dem Vergleich des Redoxpotentials des Tetrons mit dem zahlreicher anderer Stoffe, die das Gold in Gesteinen, Konzentraten oder Halbprodukten begleiten können.

Wir nahmen uns vor, dieses Verhalten des Tetrons zu verwerten, um eine empfindlichere, selektivere und zugleich weniger anspruchsvolle Methode zur Bestimmung von geringen Goldmengen zu schaffen.

EXPERIMENTELLER TEIL

Reagentien

Goldstandartlösung: 0,0250 g Gold wird in etlichen ml Königswasser aufgelöst, mittels IR-Glühlampe zur Trockne eingedampft, der Rückstand mit 1 ml Konz. Salzsäure versetzt, wieder zur Trockne eingedampft und in einem Messkolben auf 250 ml mit 1M Salzsäure verdünnt. Dieser Lösung, die 100 μg Au(III)/ml enthält, entnimmt man 10 ml, verdünnt sie mit frisch destilliertem Wasser auf 100 ml und erhält eine Lösung von 10 μg Au(III)/ml.

0,1 %*ige Tetronlösung:* 0,1 g Tetron, aufgelöst in 100 ml verd. Schwefelsäure (1:20).

0,1 %*ige Lösung von Kaliumtellurit:* 0,1 g K_2TeO_3 werden in etlichen ml 2,5M Salzsäure aufgelöst und mit Wasser auf 100 ml verdünnt.

10%*ige Zinn*(II)*-chloridlösung:* Frisch bereitete Auflösung von 10 g $SnCl_2$ in 2,5M Salzsäure unter Erhitzen.

3*M Bromwasserstoffsäure*
Äthyläther: p.a.
2,5*M Salzäure*
konz. Salzsäure; konz. Salpetersäure.

ERGEBNISSE

Eine der wesentlichsten Schwierigkeiten, auf die man bei der Bestimmung geringer Mengen von Gold stösst, ist seine Trennung. Dazu benutzt man: die Mitfällung des Goldes durch ein geeignetes Fällungsmittel (Tellur,[14] Bleisulfid,[21,22] ein Gemisch von Quecksilber-(II)-chlorid und Magnesium[20] u.a.); ferner die Extraktion des Goldes mit Äthyläther,[23,24] Isopropyläther[25] oder Äthylacetat[23] aus Chlor- bzw. Bromwasserstoff-säurem Medium und schliesslich Ionenaustausch[26] oder Adsorption über Kohle, Zellulose u.a.

Unsere Versuche zeigten, dass es bei der Aufarbeitung zusammengesetzter Proben wie Gesteine, Erze und Konzentrate am zweckmässigsten ist, das Gold zunächst durch Mitfällung mit Tellur von den Begleitelementen abzutrennen und anschliessend die Gold(III)-ionen mit Äther aus einem Medium von 3M Bromwasserstoffsäure zu extrahieren.

Bestimmung des Goldes in Kupfer-Eisen- und gemischeten Konzentraten

Analysegang: 0,5 bis 2,0 g der fein verriebenen Probe werden im Gemisch von Lunge aufgelöst. Man dampft die Lösung auf Sandbad zur Trockne ein. Einwirkenlassen von 3 bis 4 ml konz. Salzsäure auf den Rückstand mit nochmaligem Eindampfen zur Trockne. Nach Zugabe von 60 bis 70 ml der 2,5M Salzsäure und 2 ml Kaliumtelluritlösung erwärmt man fast bis zum Sieden und reduziert mit 15–20 ml Zinn(II)-chloridlösung.* Es entsteht eine dunkelbraune kolloidale Lösung von Elementartellur, die beim Liegenlassen flockig wird wobei sich das Tellur auf den Boden setzt. Der Niederschlag wird nach einer Stunde abfiltriert (Weissbandfilter) und mit 0,2M Salzsäure ausgewaschen. Das Filter wird samt Niederschlag im Porzellantiegel bei 800–900° verbrannt und geglüht. Unter diesen Bedingungen entweicht das Tellur als Oxyd, und im Tiegel verbleibt das Gold, gelegentlich mit einigen Platinmetallen, geringen Mengen von Siliciumsäure, Kupfer, Blei und Eisen vermischt. In das Becherglas, in dem die Mitfällung erfolgt war, bringt man 2 bis 3 ml Königswasser, deckt mit dem Uhrglas zu und erhitzt auf dem Sandband 15–20 Min. lang. Das Säurengemisch wird in den Tiegel eingegossen, mit Uhrglas bedeckt und 15–20 Min. erwärmt. Nach Abnahme des Uhrglases dampft man die Lösung mittels IR-Glühlampe zur Trockne ein.† Dem Trockenrückstand werden 10 ml 3M Bromwasserstoffsäure zugesetzt; nach heftigem Umrühren mit Glasstab wird die Lösung samt dem Niederschlag der Siliciumsäure in den Scheidetrichter gebracht und darin 3 Min. lang mit 10 ml Äthyläther extrahiert. Praktisch geht das Gold schon bei der ersten Extraktion in die organische Phase über. Um grössere Gewissheit zu erlangen führt man am besten eine zweite Extraktion durch.‡ Die vereinten ätherische Auszüge werden in einem 25 ml-Becherglas mit Hilfe der IR-Glühlampe langsam zur Trockne eingedampft. Auf den Rückstand lässt man 10–15 Tropfen Königswasser einwirken, dann erhitzt man 15 Min. mit aufgesetztem Uhrglas und dampft vorsichtig zur Trockne ein. Nach Versetzen mit 1 ml 0,1 % iger Tetronlösung entsteht orangegelbe Färbung, die allmählich

---

* Die Menge an Zinn(II)-chlorid muss dazu ausreichen, nicht nur das Tellur, sondern auch die vorhandenen Eisen(III)- und Kupfer(II)-ionen reduzieren zu können.

† Die Temperatur darf 70–80° nicht übersteigen, sonst könnte sich das Gold(III)-chlorid zersetzen. Die Luft darf nicht verstaubt noch verqualmt sein (kein Tabakrauch!), da Reduktion des Gold(III)-chlorids zu Elementargold eintreten könnte.

‡ Geringe Mengen an Siliciumsäure bleiben dispergiert in der Wasserphase zurück und halten an den Trichterwänden. Damit sie nicht vom Äther mitgerissen werden, giesst man diesen durch die obere Öffnung des Scheidetrichters ab.

intensiver wird. Nach 3 bis 4 Min. verdünnt man mit frisch destilliertem Wasser* auf ein angemessenes Volumen (10-, 20- oder 50 ml) und photometriert bei Blaulichtfilter.

Goldbestimmung in Bleikonzentraten

Analysengang: 0,5 bis 2,0 g der Probe werden mit 10 bis 15 ml konz. Salzsäure übergossen und bis zum Aufhören der Entwicklung von Schwefelwasserstoff erhitzt. Dann gibt man 5 bis 10 ml konz. Salpetersäure hinzu und lässt die Lösung auf dem Sandbad zur Trockne verdunsten. Der weitere Gang der Analyse ist derselbe wie bei der Analyse von Kupferkonzentraten.

Bleibt bei der Verdünnung, die der Mitfällung des Goldes mit Tellur vorausgeht, noch ungelöstes Bleichlorid zurück, so wird es nach Abfiltrierung dadurch entfernt, dass man den gesamten Niederschlag mit 15–20 ml heissem Wasser auswäscht.

Goldbestimmung im Anodenkupfer

Bei der Aufarbeitung von Proben mit einfacher Zusammensetzung, z.B. von Anodenkupfer, kann die Abrennung des Goldes mit Hilfe eines Ionenaustauschers vorgenommen werden.

Bekanntlich haftet $[AuCl_4]^-$-an-Anionit in einem ziemlich weiten pH-Intervall: von 0,1 bis 12 n HCl.[27] Auf dieser Eigenschaft beruht das von S. Hirano, A. Mizuike und Y. Yida[26] angewandte Verfahren zur Bestimmung geringer Goldmengen im Kupfer.

Bei unseren Versuchen bedienten wir uns des Ionenaustauschers Dowex II 310 mesh in Cl^--Form. Die Säule stellte ein mit Hülse versehenes Filtrierröhrchen dar,[28] das bis zur Höhe von 10 mm mit dem Ionenaustauscher gefüllt war. Durch Aufsaugen mittels Wasserstrahlpumpe wird die Ausströmungsgeschwindigkeit auf etwa 1 ml/min eingestellt.

Analysengang: 0,1 bis 0,5 g Anodenkupfer werden in 6 ml salpetersäure (1:1) aufgelöst; der Lösung setzt man 2 ml konz. Salzsäure hinzu und verdünnt mit Wasser auf etwa 20 ml. Man lässt die Lösung durch die Säule fliessen. Diese wäscht man dann mit etwa 10 ml Salzsäure (1:10) durch. Die Filtrierpapierhülse wird mit dem Glasstab aus der Säule in einen Porzellantiegel geschoben, verbrannt und auf 800° geglüht. Den kaum merklichen Rückstand versetzt man mit ein paar Tropfen Königswasser, dampft mit Salzsäure ein, setzt 1 ml Tetronlösung hinzu, verdünnt und photometriert.

Aufnahme der Standardgeraden

Die Goldkonzentration in der zu untersuchenden Probe kann nach einer vorher aufgenommenen Standardgeraden ermittelt werden. Zur Vermeidung gelegentlicher methodischer Fehler müssen die Punkte, mit deren Hilfe die Gerade aufgenommen werden soll, das Resultat der Goldbestimmung in Lösungen sein, die bestimmte Goldkonzentration aufweisen und an denen der entsprechende Analysengang angewendet worden ist.

Da Zufallsfehler während der Bestimmung unterlaufen können, wird man die wahrscheinlichste Gerade nur erhalten, wenn jeder Punkt das arithmetische Mittel aus mehreren Berechnungsaussagen ist.

In den Konzentraten schwankt der Goldgehalt meist zwischen 0,5 und 50 g/t. Aus diesem Grunde ist es zweckmässig, zwei Standdardgeraden aufzunehmen: eine für Konzentrationen von 1 bis 7 g/t und die andere für solche von 5 bis 30 g/t. Bei der ersten werden die zu photometrierenden Lösungen auf 10 ml verdünnt, bei der zweiten auf 25 ml. Benutzt wird eine Küvette von 2 cm-Stärke des absorbierenden Mediums.

BEURTEILUNG DER ERGEBNISSE

Bewertung der Genauigkeit der Methode

Im Laufe der Analyse kommen methodische Fehler vor, deren Betrag von dem gewählten analytischen Arbeitsgang abhängig ist. Das Vorliegen solcher Fehler stellten wir bei der Aufnahme der Standardgeraden unter verschiedenen Bedingungen fest: eine bei der direkten Bestimmung von Gold(III)-chlorid mit Tetron (s. Abb. 1, Gerade I), die zweite nach vorausgegangenem Haftenbleiben des Goldes am Anionit (Gerade II) und die dritte nach der Mitfällung des Goldes mit Tellur und anschliessender Extraktion des komplex an Goldbromids mit Äther (Gerade III). Der Betrag jedes den Goldmengen 2, 4, 6, 8 μg entsprechenden Punktes stellt das arithmetische

---

* Ist das Wasser nicht frisch destilliert, enthält es Mikro-organismen, durch deren reduzierende Wirkung die Entfärbung der Lösung beschleunigt wird.

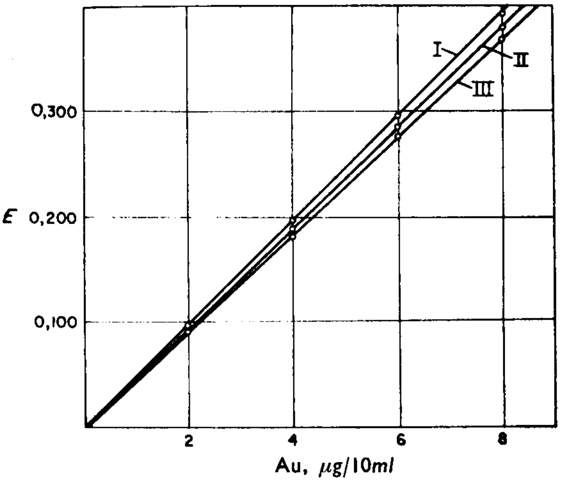


ABB. 1

Mittel aus zehn Bestimmungen dar. Die Abweichung der Geraden II and III von der Geraden I um entsprechend 2,5 oder 5,6 % besagt, dass im Gange der Analyse infolge der Unvollständigkeit der Mitfällung, der Extraktion oder des Ionenaustausches Gold teilweise verloren geht. Es leuchtet daher ein, dass es zweckmässig ist, die Aufnahme der Standardgeraden auf den jeweiligen Analysengang abzustimmen, um methodische Fehler dieser Art zu vermeiden. Ist diese Anforderung erfüllt, dann wird die Reproduzierbarkeit bzw. Genauigkeit der Methode von den unbestimmten Fehlern abhängig sein. Da diese meist aus Variationen der bestimmten Fehler herrühren, müssen sie selbst variabel sein, wie dies aus Tab. I hervorgeht.

TABELLE I

	I			II			III		
Au in 10 ml, µg	Direkte Bestimmung			Nach vorheriger Trennung von Au mit Anionit			Nach vorheriger Mitfällung von Au mit Te		
	$\bar{E}$	ς	$\frac{\varsigma}{\bar{E}} \cdot 100$	$\bar{E}$	ς	$\frac{\varsigma}{\bar{E}} \cdot 100$	$\bar{E}$	ς	$\frac{\varsigma}{\bar{E}} \cdot 100$
2	0,098	0,0018	1,8	0,095	0,0019	2,0	0,093	0,0031	3,3
4	0,195	0,0031	1,6	0,190	0,0037	1,9	0,184	0,0056	3,0
6	0,294	0,0040	1,4	0,287	0,0050	1,7	0,275	0,0068	2,5
8	0,397	0,0056	1,4	0,383	0,0060	1,6	0,372	0,0075	2,0

$\bar{E}$—arithmetischer Mittelwert der Extinktion bei $N = 10$
ς—Standardabweichung
$\frac{\varsigma}{\bar{E}} \cdot 100$—Prozentfehler

Demnach liegt der Relativfehler innerhalb der Grenzen ±7,5 bis ±4,5 %, wenn Gold einmalig in Kupfer-, Blei- oder gemischten Konzentraten mit Goldgehalt 2 bis 8 g/t bei 95 % statistischer Sicherheit bestimmt wird. Handelt es sich um Bestimmung des Goldes im Anodenkupfer, so wird sich der Relativefehler unter denselben Bedingungen auf ±3,6 bis ±4,5 % belaufen.

TABELLE II

No.	Probe	Au g/t nach photometrischer Methode	Au g/t Mittelwert	Au g/t nach der Kupellationsmeth.
1	Goldkonzentrat	60,0; 59,5; 60,0; 58,5	59,8	60,0
2	Komplexes Konzentrat	56,6; 56,6; 55,7	56,3	57,4
3	Blei/Kupfer-Konzentrat	22,0; 22,0; 23,0	22,3	23,0
4	Kupferkonzentrat No 1	8,9; 9,1	9,0	8,8
5	Kupferkonzentrat No 2	2,8	2,8	2,5
6	Bleikonzentrat	0,9; 0,8; 1,0	0,9	1,0

Anwendungsgebeit der Methode

Das Verfahren wurde bei industriellen Objekten angewendet: Gold-, Kupfer-, Blei- und gemischten Konzentraten.

Tabelle II veranschaulicht die gute Reproduzierbarkeit der Ergebnisse, die mit denen der Kupelationsmethode in Einklang stehen.

Bestimmt wurde auch der Goldgehalt im Anodenkupfer. Zur Trennung des Goldes wurden die beiden Varianten eingesetzt: einmal durch Ionenaustauscher und zum andern durch Mitfällung mit Tellur und anschliessende Extraktion.

Die erste Variation ergab bei $N = 10$; $\bar{C} = 59{,}3$ g/t; $\varsigma = 0{,}89$; $\frac{\varsigma}{\bar{C}} \cdot 100 = 1{,}5\%$.

Nach der zweiten Variante bei $N = 10$; $\bar{C} = 58{,}5$ g/t; $\frac{\varsigma}{\phi} = 1{,}25$; $\frac{\varsigma}{\bar{C}} \cdot 100 = 2{,}1\%$.

Summary—A photometric method can be used for the determination of small amounts of gold with *N,N'*-tetramethyl-*o*-tolidine (Tetron). The gold is separated by precipitation with tellurium and extraction by ether from an HBr medium, and is then treated with Tetron solution. An orange-yellow colour develops and reaches its full intensity in about 4 min. The solution is diluted, and the colour is measured using a blue filter. The colour is stable for 20–25 min, and then fades gradually. The procedure may be applied to the determination of gold in copper-, lead- and mixed-concentrates or in anode-copper. The results have been evaluated statistically.

Résumé—En vertu d'une possibilité préalablement éclaircise est proposée une méthode de determination de petites quantités d'or a l'aide de la *N,N'*-tetramethyl-*o*-tolydine (tétrone). L'or est coprécipite avec le tellure, puis extrait par l'ether en milicu bromhydrique et á la fin traité par une solution de la *N,N*-tetramethyl-*o*-tolydine. On obtient une coloration jaune orangée, qui se develloppe 4 minutes. On amene a un volume convenable et effectue la photometue en utilisant un filtre bleu, la coloration est stable 20–25 minutes, après quoi elle commence a s'affaiblir. La méthode est appliquèe a l'analyse de l'or dans des concentrés différens et dans le cuivre anodique. Les résultats sont interprétés par le calcul statistique.

LITERATUR

[1] N. Jordanov u. Ch. Daiev, *Talanta*, 1963, **10**, 163.
[2] R. Carney, *J. Amer. Chem. Soc.*, 1912, **34**, 32.
[3] J. Siemssen, *Chem.-Ztg.*, 1912, **36**, 934.
[4] I. Saul, *Analyst*, 1913, **38**, 54.
[5] H. Holzer u. W. Reif, *Z. analyt. Chem.*, 1933, **92**, 12.
[6] R. Piria, *Annalen*, 1851, **78**, 64.

[7] H. Schiff, *ibid.*, 1857, **101**, 92.

[8] I. Paulsen u. S. Pevzner, *Chem. Abs.*, 1938, **32**, 6972.

[9] F. Feigl, *Z. analyt. Chem.*, 1928, **74**, 380.

[10] N. Poluektov, *Chem. Abs.*, 1945, **39**, 3494.

[11] E. Sandell, *Analyt. Chem.*, 1948, **20**, 253.

[12] G. Malatesta u. E. di Nola, *Z. analyt. Chem.*, 1922, **61**, 184.

[13] W. Geilmann u. O. Meyer-Hoissen, *Gastechn. Ber.*, 1935, **13**, 86 (zitiert nach H. Schreiner, H. Brantner u. F. Hecht, *Mikrochim. Acta*, 1951, **36/37**, 1056.)

[14] W. Pollard, *Analyst*, 1919, **44**, 94.

[15] W. Clabaugh, *J. Res. Nat. Bur. Standards*, 1946, **36**, 119; E. B. Sandell, *Colorimetric determination of traces of metals.* Interscience, New York, Third Edition, 1959, p. 506.

[16] B. MacNulty u. L. Woollard, *Analyt. Chim. Acta*, 1955, **13**, 1955.

[17] L. Kulberg, *Zavodskaya Lab.*, 1936, **5**, 170.

[18] L. Erdey u. L. Rady, *Z. Analyt. Chem.*, 1952, **135**, 1.

[19] E. B. Sandell, *Colorimetric determination of traces of metals.* Interscience, New York, Third Edition, 1959, p. 497.

[20] *Idem, ibid.*, p. 494.

[21] F. Haber u. J. Jaenicke, *Z. anorg. Chem.* 1925, **147**, 156.

[22] F. Haber, *Z. angew. Chem.*, 1927, **40**, 303.

[23] V. Lenher u. C. Kao, *J. Phys. Chem.*, 1926, **30**, 126.

[24] R. Bock, H. Kusche u. E. Bock, *Z. analyt. Chem.*, 1953, **138**, 167.

[25] W. McBryde u. J. Yoe, *Analyt. Chem.*, 1948, **20**, 1094.

[26] S. Hirano, A. Mizuïke u. Y. Lida, *Analyt. Abs.*, 1962, **9**, 3070.

[27] R. Schuler, A. Boyd u. D. Kay, *J. Chem. Educ.*, 1951, **28**, 192; E. Blasius, *Chromatographische Methoden in der analytischen und präparativen anorganischen Chemie.* Ferd. Enke Verlag, Stuttgart, 1958, 169.

[28] N. Jordanov u. S. Dinev, *Godisnik Sof. Univ.*, 1954/1955, **2**, 19.

Talanta, 1964, Vol. 11, pp. 507 to 514. Pergamon Press Ltd. Printed in Northern Ireland

PHASE TITRATIONS—III*

NEW APPLICATIONS AND THE PHASE TITRATION OF BINARY SOLUTIONS OF CHEMICALLY SIMILAR COMPONENTS

D. W. ROGERS, A. ÖZSOĞOMONYAN and A. SÜMER
Department of Chemistry, Robert Kolej, Bebek, Istanbul, Turkey

(*Received* 29 *July* 1963. *Accepted* 20 *August* 1963)

Summary—Results are given for the phase titration of 27 new binary solutions of the water-immiscible components dichloromethane, cyclohexane, allyl bromide, benzene, toluene and xylene in combination with the water-miscible components methanol, ethanol, isopropanol, dioxan, acetone and acetic acid. A new method for the phase titration of binary solutions of liquids which are chemically similar is described. Results are given for the phase titration of binary solutions of the chemically similar liquids methyl aniline–aniline, nitrobenzene–aniline, carbon tetrachloride–chloroform, n-butyl bromide–n-butyl acetate and cyclohexane–benzene. Sampling procedures and sources of error are discussed.

MOST of the titrations of binary solutions reported in this series depend on great differences in solubility of the components. For example, solutions of carbon tetrachloride, which is completely immiscible with water, and methanol, which is completely miscible, can be analysed using water as a titrant. Part of this work has been devoted to extending the original technique to 27 new systems of this kind.

Bogin[1] showed that it is possible to take advantage of differences in solubility even when the components of a binary solution are chemically similar. Thus he was able to titrate solutions of butanol in propanol because of the partial immiscibility of butanol with water.

We will describe a method for the analysis, by phase titration, of binary solutions made up of components which are not only chemically similar but also have almost identical solubilities in water. The method is so sensitive to slight differences in solubility characteristics that it is possible to analyse solutions of chloroform in carbon tetrachloride and solutions of cyclohexane in benzene.

The new technique, like the old one, is capable of extremely wide application.

THEORY

Consider, as an illustrative binary solution, carbon tetrachloride and chloroform (solubilities: 0·077 and 0·822 g/100 ml of water respectively[2]). The phase titration of each in combination with water-miscible organic liquids has been reported.[3,4] Although they are both regarded as being completely immiscible with water, the solubility curve of the carbon tetrachloride-ethanol-water phase diagram is slightly higher than the solubility curve of the chloroform-ethanol-water phase diagram[5] as shown in Fig. 1.†

It has been shown[3] that a higher solubility curve gives a lower phase-titration calibration curve and *vice versa*. This is shown in Fig. 2. In the discussion that

---

* Part II, *Talanta*, 1963, **10**, 633.

† In the actual experiment described, acetic acid was used instead of ethanol but the principle is the same. Ethanol is referred to in this discussion because the phase diagrams are readily available.

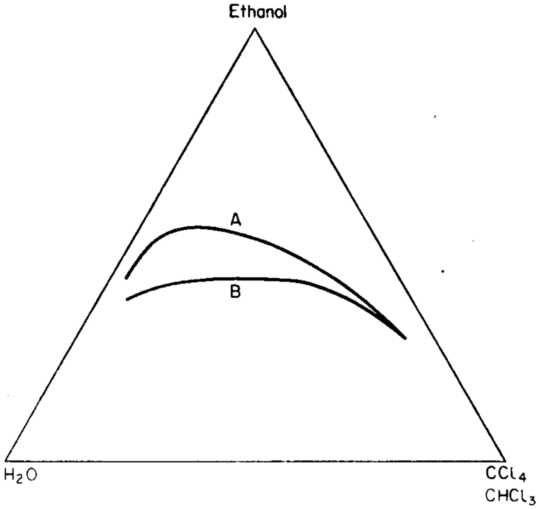


FIG. 1.—Ternary phase diagrams at 0°
A: carbon tetrachloride–ethanol–water:
B: chloroform–ethanol–water.
Taken from the International Critical Tables.[5]

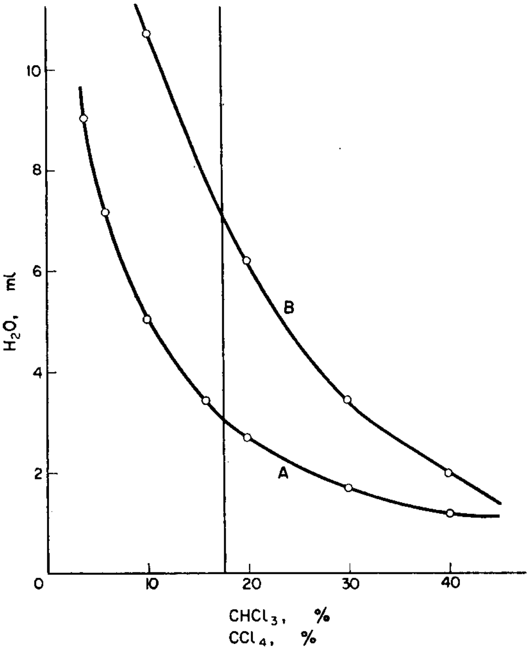


FIG. 2.—Type A solubility curves
A: carbon tetrachloride–ethanol,
B: chloroform–ethanol,
titrated with water.
The vertical line segment represents a constant composition with respect to ethanol.

follows, phase-titration calibration curves of the kind shown in Fig. 2 will be referred to as Type A solubility curves.

If, instead of titrating binary solutions of ethanol and immiscible component with water, one titrates ternary solutions of carbon tetrachloride, chloroform and ethanol with water, the titres will fall in the area between the Type A solubility curves shown in Fig. 2. The locus of the number of ml of water necessary to cause turbidity, as a function of the composition of the three component system titrated, is the three-dimensional surface shown in Fig. 3. The Type A solubility curves are the XZ plane and the outer edge of the solubility surface which is parallel to it. Notice that the concentration of water necessary to cause turbidity as a function of three other composition variables is not a surface in four dimensions because, of the four composition variables, only three are independent.

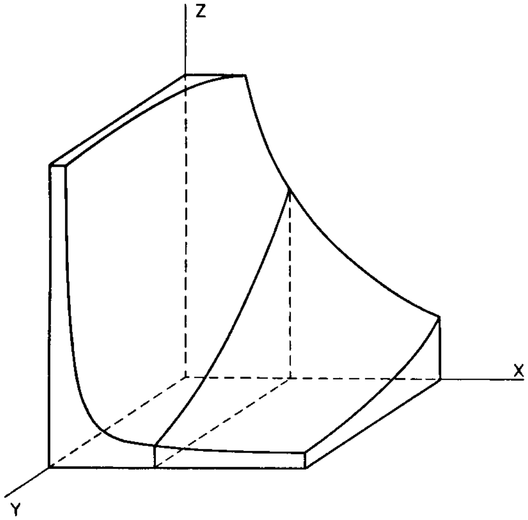


FIG. 3.—The solubility surface for the ternary system carbon tetrachloride–chloroform–ethanol titrated with water.

The axes are: X, 100 – % ethanol; Y (ml of carbon tetrachloride/ml of carbon tetrachloride + ml of chloroform), 100, *i.e.*, % carbon tetrachloride before the addition of any ethanol or water; and Z, ml of water necessary to cause turbidity.

The vertical plane parallel to the YZ plane shown in the diagram indicates constant ethanol composition.

Now simplify the problem by holding the amount of ethanol constant and allowing variation in the ratio of carbon tetrachloride to chloroform. Let the constant composition of ethanol be represented by the vertical line in Fig. 2. This line and an intersecting line perpendicular to the plane of the page define a plane. The plane so defined intersects the solubility surface as shown in Fig. 3. Its projection on the YZ plane is Fig. 4, the number of ml of water necessary to cause turbidity as a function of carbon tetrachloride percentage at constant amount of ethanol. Fig. 4 will be referred to as a Type B solubility curve. Its use as a calibration curve for the phase titration of binary solutions of carbon tetrachloride and chloroform is described in detail in the Experimental section.

The projection of the Type B solubility curve on its vertical axis gives the vertical line segment between the two Type A solubility curves in Fig. 2. The intersection of

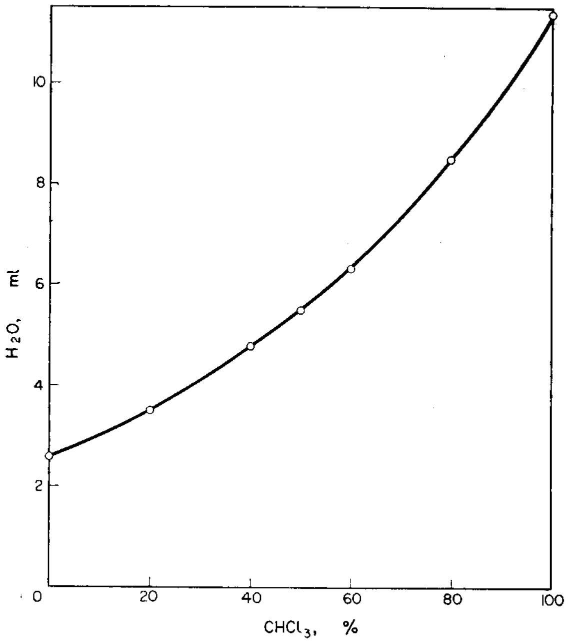


FIG. 4.—Type B solubility curve for the system carbon tetrachloride–chloroform. The horizontal axis represents the % chloroform before addition of ethanol.

the vertical line segment with the Type A solubility curves gives the upper and lower limits of the Type B solubility curve, *i.e.*, 0% and 100%. The greater the separation of the Type A solubility curves, the greater will be the slope of the Type B solubility curve and the greater will be the accuracy of any determination which depends on it.

The separation of the Type A solubility curves depends on the following factors:

The nature of the immiscible component is of prime importance.

The amount of miscible component added determines the position of the vertical line in Fig. 2. Sometimes advantage can be taken of flat portions and bulges in the Type A solubility curves to achieve a wider separation. Generally, the Type A solubility curves converge as they approach the horizontal axis, so that a wider separation is achieved at higher proportions of the miscible component. On the other hand, the end-point is usually sharper at lower proportions of the miscible component. There is an optimum proportion of miscible component which best satisfies both of these conditions.

Shifting the position of the vertical line in Fig. 2 also determines the size of the titre. It is generally best placed so that the limits of the Type B solubility curve are about 1 and 12 ml.

Doubling the sample size doubles each titre and doubles the separation of the Type A curves. Thus, advantage can be taken, by appropriate increase in the sample size, of subtle differences in the solubility characteristics of the substances titrated.

There are exceptions to this rule, but inspection of over one hundred Type A solubility curves showed that the miscible component has little effect on the separation of the curves. Factors of availability and price were most important in determining the choice of the miscible component, and we expect that a change in the miscible component in the systems reported in Table II would have little effect on the results.

Bogin[1] has suggested, but not carried out, the application of this principle to analogous systems in which the ratio of two completely water-miscible components can be determined by phase titration with water in the presence of a constant amount of a water-immiscible or slightly water-miscible component. He suggests that ethanol–propanol mixtures can be titrated with water in the presence of a constant amount of butanol. Bogin has also devised a method for the titration of chemically similar components using as the titrant, not water, but binary and even ternary solutions in which one of the components is water. Such a method involves titration surfaces like the one shown in Fig. 3, but is less easily visualised because the addition of titrant causes a variation in two or even three of the composition variables. The selection of the composition of the mixed solvent titrant was empirical. The disadvantages involved in the use of a mixed-solvent titrant, which must be exactly the same in composition from one titration to the next, as contrasted to water, which never need be standardised, are discussed by Bogin.

EXPERIMENTAL

Reagents

Reagent-grade carbon tetrachloride and benzene were obtained from E. Merck A. G., Darmstadt. Reagent-grade aniline and xylene were obtained from Mallinckrodt Chemical Works, New York and reagent-grade nitrobenzene from Fischer Scientific Co., Fair Lawn, N.J. Technical methyl aniline was obtained from Amend Drug and Chemical Co., New York, and practical-grade cyclohexane from Eastman Organic Chemicals, Rochester, N.Y.

TABLE I.—RESULTS FOR THE TITRATION OF 27 HOMOGENEOUS BINARY SYSTEMS WITH WATER, The end-point was indicated by the appearance of a distinct permanent turbidity.

Sample	Optimum range, %	Number of titrations	Average error, *absolute* %
Dichloromethane-methanol	13–50	9	0·21
Dichloromethane-ethanol	15–50	12	0·19
Dichloromethane-isopropanol	17–38	6	0·23
Dichloromethane-dioxan	7–22	12	0·19
Dichloromethane-acetone	6–20	10	0·22
Dichloromethane-acetic acid	15–50	14	0·23
Cyclohexane-methanol	1–10	12	0·10
Cyclohexane-ethanol	1–20	12	0·06
Cyclohexane-isopropanol	5–45	12	0·04
Cyclohexane-dioxan	1–15	12	0·13
Cyclohexane–acetone	1–25	12	0·03
Cyclohexane–acetic acid	1–7	12	0·05
Allyl bromide-methanol	4–35	12	0·01
Allyl bromide-ethanol	5–40	15	0·05
Allyl bromide-isopropanol	10–45	12	0·08
Allyl bromide-dioxan	4–25	12	0·07
Allyl bromide-acetone	3–20	12	0·09
Allyl bromide-acetic acid	5–30	12	0·22
Benzene-dioxan	3–20	12	0·05
Benzene-acetone	4–25	12	0·05
Benzene-acetic acid	5–30	12	0·06
Toluene-dioxan	2–20	12	0·04
Toluene-acetone	3–23	12	0·16
Toluene-acetic acid	2–25	12	0·06
Xylene-dioxan	1–20	6	0·09
Xylene-acetone	2–25	12	0·04
Xylene-acetic acid	2–20	12	0·11

Chemicals of unspecified grade were toluene and dichloromethane (density 1·322–1·324) from E. Merck; and allyl bromide (3-bromopropene, b.p. 70–71°, lot no. 370220) from Matheson Coleman and Bell, New Jersey. All other reagents have been described elsewhere, and their sources given.[6]

Sampling procedure

Aliquot portion method: An appropriate volume of the water-insoluble or least water-soluble component was pipetted into a 50-ml volumetric flask and diluted to the mark with the water-soluble or most water-soluble component. For example, in Table I, cyclohexane was diluted to the mark with methanol; and in Table II carbon tetrachloride was diluted to the mark with chloroform. Aliquot portions (10 ml unless otherwise noted) were withdrawn for titration with water. The first was arbitrarily taken as a point on the calibration curve and the remaining three were taken as synthetic unknowns.

TABLE II.—RESULTS FOR THE TITRATION OF 5 HOMOGENEOUS BINARY SYSTEMS WITH WATER
A soluble component was added to each before titration

Sample	Soluble component added	Sample taken, *ml*	Soluble component added, *ml*	No. of titrations	Average error, *absolute* %
Methylaniline–aniline	Ethanol	10	10	12	0·16
Carbon tetrachloride–chloroform	Acetic acid	10	25	10	0·65
n-Butyl bromide– n-butyl acetate	Ethanol	10	15	10	1·0
n-Butyl bromide– n-butyl acetate	Ethanol	10	15	9	0·32
Nitrobenzene-aniline	Ethanol	10	10	12	0·43
Cyclohexane-benzene	90% ethanol 10% water	3	25	15	1·1
Cyclohexane-benzene	Ethanol	5	25	15	0·59

Individual portion method: An appropriate volume of each component was measured into a titration vessel. The volume percentage of the least soluble component was calculated, disregarding volume changes caused by mixing. Alternatively, weight percentages could have been used. After constructing the calibration curve, synthetic unknowns were prepared by the same method and determined by comparison. Compositions of the synthetic unknowns were, in most cases, different from the solutions used to construct the calibration curve.

Titration procedure

The results in Table I were obtained as described in the first paper of this series.[3]

The data in Table II were obtained by placing 3–10 ml of the unknown binary solution in a beaker and diluting with 10–25 ml of a liquid miscible with water and both components of the solution to be analysed. The amount of each liquid used, and the miscible component chosen are given in Table II. The criteria for the choice of the miscible component are maximum separation of the Type A solubility curves and a sharp end-point. The criteria for choosing the amount of miscible component are similar: maximum separation of the solubility curves consistent with a good end-point and a convenient titre. The criteria for good end-points have been discussed elsewhere.[4]

The ternary solution so obtained is then titrated with water. The behaviour of the solution during titration and the end-point is in all respects similar to the phase titration of binary solutions with water. A Type B solubility curve is constructed from known samples, and synthetic unknowns are determined by comparison.

Calculations

The calculations are straightforward, except that in the single sample method, if the final volume of all the samples is not the same, they must be normalised to one another. Thus, if one sample is made up by adding 2 ml of one component to 10 ml of the other, and if the second sample is made up by adding 3 ml to 10 ml. the titres could be normalised by multiplying the second by 12/13.

RESULTS AND DISCUSSION

Table I shows the results of the titration of 27 binary systems containing one water-miscible component. All end-points are fair to good except cyclohexane-acetic acid and allyl bromide-acetone. Even those titrations with fair or poor end-points gave small errors because the calibration curves are steep in the optimum titration range.

Table II shows the results for 5 binary systems both components of which are insoluble in water. The maximum titre was 10–15 ml, and the separation of the 0% and 100% titres was about 10 ml. The two series of determinations on the system n-butyl bromide–n-butyl acetate only differed in that the first was by the single sample method and the second by the aliquot portion method. A mixed solvent was added to the first of the cyclohexane-benzene systems to bring the titre into a more convenient range. All end-points were good to excellent with the exception of the first cyclohexane-benzene system, which was fair to poor. All systems in Table II showed a gradual opalescence followed by a sharp turbidity. This effect has been discussed before[6] but was much more noticeable in the systems given in Table II than in any other systems we have studied. The end-point is similar to, but not identical with, the end-point of a 100% sample of the less soluble of the two components. All calibration curves increased in slope with increasing titre, as shown in Fig. 3.

Errors

Of the systems given in Table I, those in which dichloromethane is one of the components were done by the single sample method, and the others were done by the aliquot portion method. The error reported for the latter may be called titration error, and largely results from uncertainty in the end-point. The error reported for the dichloromethane systems is the sum of the titration error, the errors arising from sample mixing and measurement and the errors resulting from interpolation between points on the calibration curve. In principle, these sources of error can be reduced to any desired level by more sophisticated measuring techniques and more points on the calibration curve. The two systems containing n-butyl bromide in Table II have the same relationship as that described above.

If many points are to be taken on the calibration curve, it may become tedious to construct a new curve each time there is an appreciable temperature change. The use of a constant-temperature room has the advantage in convenience over the use of a thermostatted bath. Even though heat of mixing causes temperature fluctuations, these effects will cancel between the unknown and the calibration curve (all other factors being constant). Sensitivity to temperature change varies considerably from one system to another.

The last two series in Table II show the effect of curve separation and end-point quality on accuracy.

In the penultimate determination, the difference in titres was about 11 ml, but in order to achieve that separation the composition line intersected the Type A solubility curves where they were very steep. We have seen[4] that most systems have the best end-point on the flat of their Type A solubility curves.

The final entry in Table II shows the same determination at a lower relative ethanol concentration. The difference between maximum and minimum titres has been reduced to 9·5 ml but the end-point has been improved and the error considerably reduced.

Acknowledgment—The authors gratefully acknowledge a grant by the Society of Sigma Xi in support of this research. We thank Tuğrul Yasar for help with the calculations.

Zusammenfassung—Ergebnisse der Phasentitration 27 neuer binärer Lösungen mit den wasserunlöslichen Komponenten Dichlormethan, Cyclohexan, Allylbromid, Benzol, Toluol und Xylol und den wasserlöslichen Komponenten Methanol, Äthanol, Isopropanol, Dioxan, Aceton und Essigsäure werden angegeben. Eine neue Methode für die Phasentitration binärer Lösungen chemisch ähnlicher Flüssigkeiten wird beschrieben. Ergebnisse werden für die Phasentitration binärer Lösungen der chemisch ähnlichen Flüssigkeitspaare Methylanilin-Anilin, Nitrobenzol-Anilin, Tetrachlorkohlenstoff-Chloroform, n-Butylbromid-n-Butylacetat und Cyclohexan-Benzol angegeben. Verfahren zur Probenahme und Fehlerquellen werden diskutiert.

Résumé—On donne les résultats de la détermination de la composition des phases de 27 nouveaux mélanges binaires de liquides non miscibles à l'eau: dichlorométhane, cyclohexane, bromure d'allyle, benzène, toluène et xylène combinés à des liquides miscibles à l'eau: méthanol éthanol, isopropanol, dioxanne, acétone et acide acétique. Une nouvelle méthode pour la détermination de la composition des phases de mélanges binaires de liquides qui sont chimiquement analogues est décrite. On donne les résultats de la détermination de la composition des phases de mélanges binaires de liquides chimiquement analogues: méthylaniline-aniline, nitrobenzène-aniline, tétrachlorure de carbone-chloroforme, bromure de n-butyle-acétate de n-butyle et cyclohexane-benzène. Les méthodes d'échantillonnage et les causes d'erreur sont discutées.

REFERENCES

[1] C. D. Bogin, *Ind. Eng. Chem.*, 1924, **16**, 380.
[2] *Organic Solvents.* Vol. VII in A. Weissberger *et al.*, *Techniques of Organic Chemistry*, 2nd editon. Interscience, New York, 1955.
[3] D. W. Rogers, *Talanta*, 1962, **9**, 733.
[4] D. W. Rogers and A. Özsoğomonyan, *ibid.* 1963, **10**, 633.
[5] *International Critical Tables*, Vol. III, p. 410, Fig. 11, 13.
[6] D. W. Rogers and A. Özsoğomonyan, *Talanta*, 1964, **11**, 652.

Talanta, 1964, Vol. 11, pp. 515 to 521. Pergamon Press Ltd. Printed in Northern Ireland

LE TITRAGE ENTHALPIMETRIQUE DE QUELQUES REACTIFS ORGANIQUES SOUFRES UTILISES EN CHIMIE ANALYTIQUE

E. Popper, L. Roman et P. Marcu
Département de Chimie Analytique de la Faculté de Pharmacie Cluj, Rumania

(*Reçu le* 29 *Juillet* 1963. *Accepté le* 7 *Septembre* 1963)

Résumé—Dans le présent travail on a appliqué la méthode de titrage enthalpimétrique de deux réactifs organiques soufres, le 2-mercapto-5-anilino-1,3,4-thiodiazol et l'allylmonoamide de l'acide hydrazin-*N,N'*-bisthiocarbonique, qui ont un caractère très faiblement acide. On a appliqué une technique manuelle discontinue, et dans le cas de l'allyl-monoamide de l'acide hydrazin-*N,N'*-bisthiocarbonique on a procédé à une transformation des coordonnées droites en coordonnées obliques, afin d'écarter l'influence des processus secondaires sur l'effet thermique de la réaction de neutralisation. A partir des données expérimentales on a calculé aussi les chaleurs de neutralisation de ces réactifs par l'hydroxyde de sodium.

PRINCIPE DE LA MÉTHODE

Toute réaction chimique est accompagnée d'une variation de l'enthalpie du système, ainsi que l'attestent les effects thermiques qui ont lieu pendant la réaction. De ce fait, des renseignements précieux peuvent être obtenus sur une réaction chimique par la connaisance des échanges thermiques au cours de la réaction.

La méthode de titrage enthalpimétrique a été l'objet de modifications, tant en ce qui concerne la dénomination que la technique de travail. A l'origine, cette méthode était nommée "titrage thermique" ou "titrage thermométrique" et la quantité de chaleur dégagée était déterminée calorimétriquement.[1]

La détermination calorimétrique de la quantité de chaleur dégagée au cours d'une réaction chimique implique certaines difficultés. Dutoit et Grobet[2] ont remplacé la détermination calorimétrique de la quantité de chaleur par la mesure des variations de température. Par ailleurs, par la différence de titrage potentiométrique, on évalue l'énergie libre au moyen de la réaction:

$$\Delta F = -\varepsilon z F y$$

(ε = f.e.m. de la pile, z = nombre d'équivalents qui participent au transport du courant électrique, Fy = constante de Faraday).[3]

Les titrages enthalpimétriques mettent en évidence d'une part l'énergie libre et d'autre part l'entropie du système, en vertu de la relation:

$$\Delta H = \Delta F + T\Delta S$$

(ΔH = variation de l'enthalpie, respectivement du contenu calorique, ΔF =variation de l'énergie libre, ΔS = variation de l'entropie, T = température absolue).

Il en résulte avec évidence pourquoi la notion de "titrage thermique" ou de "titrage thérmométrique" a été remplacée par celle de "titrage enthalpimétrique". En outre, cette notion rend mieux compte de la méthode.

TECHNIQUE DE TRAVAIL

Ainsi que nous le signalions, la technique de travail a subi elle aussi des modifications au long des années. C'est ainsi que de la détermination calorimétrique de la quantité de chaleur on est passé à la détermination de la variation de température. Cela est réalisable soit à l'aide d'un thermomètre différentiel Beckmann, soit d'un thermistor.

Il importe que ces titrages soient effectués dans des vases thermiquement isolés—Dewar—, avec des dispositifs de titrage également isolés, que l'on ajoute des quantités égales de réactif à des intervalles de temps égaux et que l'on mesure la température avec toute la précision possible. On représente graphiquement la variation de température, en fonction des ml. de réactif additionnés, tandis que la courbe obtenue représente le titrage enthalpimétrique, dans le processus donné.

Dans les installations modernes, réalisées par certains chercheurs,[4,5] on effectue les titrages enthalpimétriques à l'aide de burettes à écoulement constant, tandis que la variation de la température est enregistrée par un thermistor et la courbe de titrage se trace avec un enregistreur potentiométrique.

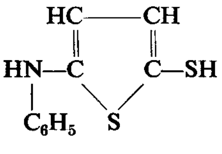
La technique utilisée par nous a été la suivante: un vase Dewar, isolé lui aussi par précaution, une burette Schelbach de grande précision introduite dans un manchon de verre, afin de réaliser l'isolation thermique par la couche d'air formée de la sorte, un thermomètre Beckmann, et pour l'agitation continue et constante un agitateur électromagnétique du type I.O.R. (R.P.R.). Pour la lecture des millièmes de degré nous avons utilisé une loupe. Avant la détermination on vérifie les températures des solutions contenues dans la burette et le vase Dewar à l'aide d'un thermomètre décimal. La différence entre les températures de la solution à titrer et la solution titrante ne doit pas être plus grande que 0,3°C. La pointe de la burette doit être effilée et isolée, et elle s'introduit dans le vase Dewar par un bouchon en liège, tout comme le thermomètre Beckmann.

Les déterminations doivent être faites dans une pièce où les variations de température soient minimales; les solutions y sont abandonnées pendant une heure environ pour permettre l'équilibre de la température avec celle du milieu ambiant.

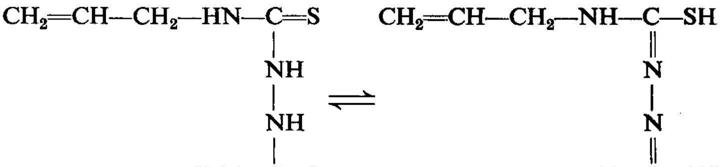
APPLICATION DE LA MÉTHODE

Cette méthode physico-chimique peut être appliquée à l'étude de beaucoup de réactions chimiques, parmi lesquelles nous signalons: la neutralisation des acides polybasiques, le déplacement des acides faibles de leurs sels avec des bases fortes, la précipitation des hydroxydes métalliques, la formation des hydroxydes amphotères, la formation des sels basiques, diverses précipitations analytiques, la formation de complexes, réactions d'oxydation-réduction, sulfonations, titrages[6] ainsi le titrage de certains alcaloides.[7] Contrairement aux méthodes de volumétrie physico-chimique, conductivités électriques et sauts de potentiel, comme indicateurs, cette méthode n'est pas assez précise pour un dosage analytique.

Dans le présent travail, nous rapportons une étude enthalpimétrique de la réaction de neutralisation de quelques réactifs organiques soufrés, à savoir le 2-mercapto-5-anilino-1,3,4,-thiodiazol (I) et l'allyl-monoamide de l'acide hydrazin-*N*,*N'*-bisthiocarbonique (II), par de l'hydroxyde de sodium:



(I)



$$CH_2{=}CH{-}CH_2{-}HN{-}C({=}S){-}NH{-}NH{-}C({=}S){-}NH_2 \rightleftharpoons CH_2{=}CH{-}CH_2{-}NH{-}C(SH){=}N{-}N{=}C(SH){-}NH_2$$

(II)

la forme cétonique — la forme énolique

Cette étude vient compléter celles effectuées avec ces réactifs en vue d'élaborer de nouvelles méthodes gravimétriques rapides, colorimétriques, etc.,[8] pour le dosage des divers cations, ainsi que les recherches tendant a remplacer l'hydrogène sulfuré comme réactif analytique.

Compte tenu du fait que ces réactifs ont un caractère faiblement acide, en raison de l'influence que l'atome de soufre exerce sur l'hydrogène qui lui est lié ou qui est voisin, nous avons cru utile de proceder au titrage enthalpimétrique, afin de déceler le comportement de ces réactifs dans certaines réactions. Cela est d'autant plus utile qu'il est bien connu que l'on titre difficilement les acides très faibles par la titrimétrie habituelle. Dans le cas des acides bibasiques très faibles, le second palier de dissociation ne peut pas même être mis en évidence. Or, on verra que, par cette méthode, dans le cas de L'allyl–amide on peut mettre en évidence le deuxieme palier de dissociation. On a calculé aussi la chaleur de neutralisation dans le cas des deux réactifs.

RÉSULTATS DES EXPERIENCES

A. *Détermination de la constante enthalpimétrique de la cellule*

Avant d'effectuer un titrage enthalpimétrique, il importe de déterminer expérimentalement la constante enthalpimétrique de la cellule où l'on fait le titrage, en utilisant la relation:

$$Q = \mathrm{Nm}\frac{\Delta H}{\Delta T_Q}$$

où:

Q = la constante enthalpimétrique de la cellule,
Nm = nombre de mols du produit formé,
$\Delta H = \Delta H^\circ = 13{\cdot}4$ kcal/mol,

ΔT_Q = la variation totale de température, à la neutralisation de 250 ml de HCl. 0·01*M* par une solution d'hydroxyde de sodium 1*M*. Pratiquement, on place dans la cellule 250 ml de HCl 0·01*M* et on titré par de l'hydroxyde de sodium 0·1*M* en ajoutant un ml. de minute en minute. Cicontre (fig. 1) est représentée la courbe de titrage enthalpimétrique de l'acide chlorhydrique par de l'hydroxyde de sodium, qui permet de déterminer la constante enthalpimétrique de la cellule de titrage.

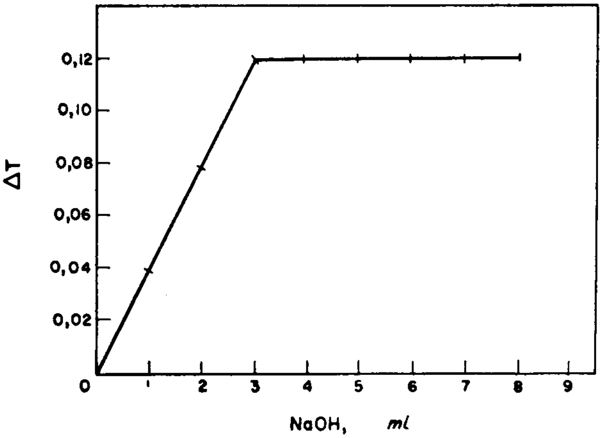


FIG. 1

Si $\Delta H = \Delta H^\circ = 13{\cdot}4$ kcal/mol, $\Delta T_Q = 0{\cdot}12$°C et Nm = 0·003063, la constante enthalpimétrique a la valeur:

$$Q = \mathrm{Nm}\frac{\Delta H}{\Delta T_Q} = 0{\cdot}003063\,\frac{13{\cdot}4}{0{\cdot}12} = 0{\cdot}34205 \text{ kcal/°C}.$$

B. *Titrage enthalpimétrique du 2-mercapto-5-anilino-*1,3,4,*-thiodiazol*

Ce réactif a une fonction mercapto dont l'atome d'hydrogène peut être remplacé par des métaux. Comme nous venons de le dire, ce réactif a été employé pour le dosage pour divers cations (Ag^+, Pb^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Bi^{3+}).

Ce réactif a été titré en solution $M/334{\cdot}4$ par une solution $0{\cdot}1M$ d'hydroxyde de sodium, en ajoutant à 300 ml de réactif, 2,5 ml d'hydroxyde de sodium par minute. Le réactif étant insoluble dans l'eau on a préparé aussi bien le réactif que l'hydroxyde en solutions alcooliques (50% alcool). Ce fait est particulièrement important parce que, lorsqu'on travaille avec une solution alcoolique de réactif et une solution aqueuse d'hydroxyde, l'effet thermique de la dilution de l'alcool est beaucoup plus grand que celui de la réaction. La courbe de titrage pour ce cas est représentée dans la fig. 2, où est consignée la variation de température ΔT, en fonction du volume de réactif ajouté. Il ressort du graphique, comme prenu que dans l'intervalle A-B la température varie de manière linéaire. Au point B, qui normalement devrait correspondre au point d'équivalence, la température demeure constante, et l'on obtient un palier horizontal parallèle à l'axe des abscisses.

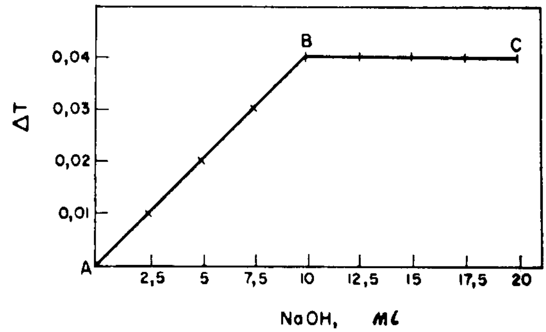


FIG. 2

Nous avons essayé d'appliquer la méthode à des dosages, mais pour de petits volumes d'hydroxide (0·5–1 ml) la variation de témperature est très petite, surtout autour du point d'équivalence, parce que ce réactif est un acide très faible.

Puisque dans ce cas $\Delta T = 0{\cdot}04^\circ C$, $Q = 0{\cdot}34205$ et $Nm = 0{\cdot}00099135$, dans cette réaction la chaleur de neutralisation est:

$$\Delta H = \frac{Q}{Nm} \,.\, \Delta T = \frac{0{\cdot}34205}{0{\cdot}00099135} \,.\, 0{\cdot}04 = -13{\cdot}801 \text{ kcal/mol.}$$

C. *Titrage enthalpimétrique de l'allyl-monamide de l'acide hydrazin N,N'-bisthiocarbonique*

Avec ce réactif, le titrage enthalpimétrique est plus utile et plus intéressant parce que, ayant deux fonctions mercapto d'un caractère acide plus faible ($K_1 = 1{\cdot}437 \,.\, 10^{-11}$), la méthode offre la possibilité de mettre en évidence le second palier de dissociation.

Dans ce cas aussi nous avons travaillé avec des solutions alcooliques (50% alcool) de réactif et d'hydroxyde en plaçant dans la cellule 200 ml de réactif $M/29{\cdot}996$, et ajoutant de minute en minute 2 ml NaOH env. $1M$.

La courbe de titrage est consignée dans la fig. 3, où on a representé graphiquement les variations de température au cours du titrage (ΔT) en fonction du volume d'hydroxyde de sodium ajouté. Il ressort du graphique que la température varie de manière

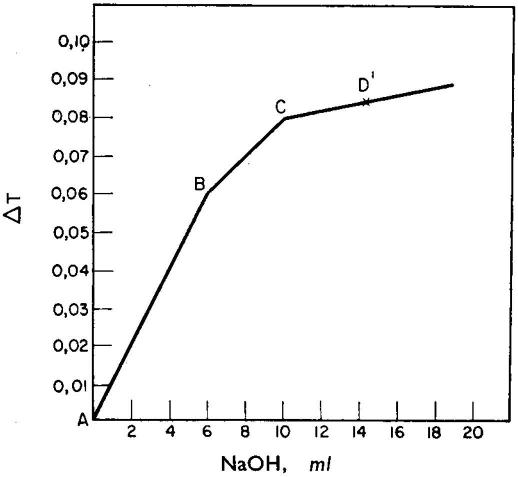


FIG. 3

linéaire dans l'intervalle A-B. Cette portion de la courbe correspond à la neutralisation du premier atome d'hydrogène. A partir du point B, la pente de la courbe se modifie brusquement, la température variant également de manière linéaire sur la portion B-C, qui correspond en réalité au titrage du deuxième atome d'hydrogène. A partir du point C, la pente de la courbe se modifie de nouveau, la température variant de manière linéaire lorsqu'on ajoute l'excès d'hydroxyde.

Afin d'écatrer l'effet thermique qui résulte du mélange de deux liquides à des température relativement différentes, un système de coordonnées obliques, *ayant les niveaux en* ordonnée inclinés avec la pente a été adojté:

$$p = \frac{\Delta T}{\Delta n}.$$

La courbe de titrage transposée sur les nouvelles coordonnées est représentée fig. 4.

On remarque que cette représentation met en évidence seulement la variation de température déterminée par le procès de neutralisation, en éliminant l'influence des

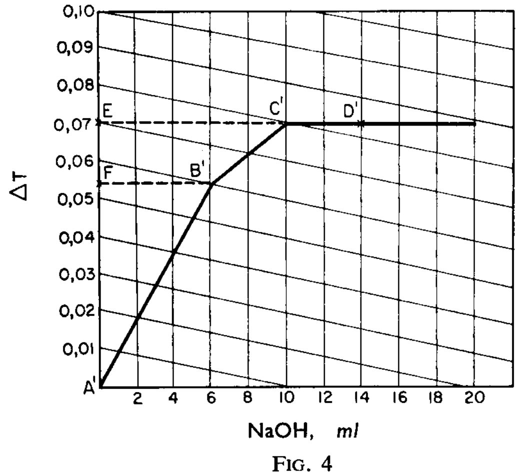


FIG. 4

phénomènes secondaires. Ce fait ressort avec évidence lorsqu'on prolonge le segment C'D' et que l'on trace une parallèle à l'abscisse par B', ce qui détermine sur l'ordonnée les points E et F correspondant à la variation de température due uniquement au processus de neutralisation.

On passe aux coordonnées obliques à l'aide des équations de transformation suivantes:

$$Y = y - px$$

$$X = x\sqrt{1 + p^2}$$

où:

X et Y sont les coordonnées du nouveau système de représentation, x et y les coordonnées de l'ancien système, et p la pente de la dernière portion de la courbe.

Les coordonnées des points B et C dans le système de coordonnées droites sont $x_B = 6$, $y_B = 0{\cdot}06$, la pente du segment CD, $p = \frac{\Delta T}{\Delta n} = \frac{0{\cdot}04}{4} = 0{\cdot}01$, et après la transformation en coordonnées obliques, les coordonnées des points B' et C' sont:

$$X_B' = 6\sqrt{1 + 0{\cdot}0001} = 6\varepsilon$$

$$Y_B' = 0{\cdot}060 - 0{\cdot}006 = 0{\cdot}054$$

$$X_C' = 10\sqrt{1 + 0{\cdot}0001} = 10\varepsilon$$

$$Y_C' = 0{\cdot}08 - 0{\cdot}01 = 0{\cdot}07.$$

Etant donné que l'accroissement ε a de X_B, et X_C, par la transposition en coordonnées obliques est très petit on le néglige, de sorte que ces coordonnées restent pratiquement les mêmes; en revanche, la diminution de Y_B, et Y_C, est sensible.

En ce qui concerne la chaleur de neutralisation, on la calcule comme dans le cas du titrage du 2-mercapto-5-anilino-1,3,4-thiodiazol au moyen de la relation:

$$\Delta H = \frac{Q}{Nm} . \Delta T .$$

Compte tenu du fait que la valeur de la constante enthalpimétrique de la cellule est $Q = 0{\cdot}34205$, $\Delta T_1 = 0{\cdot}054$, $\Delta T_2 = T - T_1 = 0{\cdot}07 - 0{\cdot}054 = 0{\cdot}016$ et que $Nm_1 = Nm_2 = 0{\cdot}00337$, les valeurs des chaleurs de neutralisation pour les deux paliers de la réaction sont:

$$\Delta H_1 = -5{\cdot}5403 \text{ kcal/mol}$$

$$\Delta H_2 = -1{\cdot}6417 \text{ kcal/mol}$$

CONCLUSIONS

1. Le titrage enthalpimétrique du 2-mercapto-5-anilino-1,3,4-thiodiazol et de l'allyl-monoamide de l'acide hydrazin-*N*,*N'*-bisthiocarbonique par de l'hydroxyde de sodium démontre l'allure des réactions de neutralisation, et dans le cas du dernier réactif permet de mettre en évidence le second palier de dissociation (par la transposition de la courbe en coordonnées obliques).

2. La méthode permet de calculer les chaleurs de neutralisation dans le cas des deux réactifs, après la détermination préalable de la constante enthalpimétrique de la cellule.

3. En dépit des essais que nous avons faits, la méthode n'a pas pu être utilisée pour des déterminations quantitatives; Nous pensons néanmoins y parvenir en modifiant la technique de travail.

4. Ce travail constitue le commencement d'une étude physico-chimique de ces réactifs qui ont été étudies et utilisés à des fins analytique. Nous aurons en vue, par suite, d'etudier le problème de la structure des combinations que ces réactifs forment avec les cations lourds.

5. En ce qui concerne l'établissement des équations de transformation en coordonnées obliques, les auteurs ont joui de l'aide précieuse que leur a accordée l'Institut de calcul de L'Académie de la R.P.R. Cluj, auquel ils adressent par cette voie leurs plus vifs remerciements.

Summary—Enthalpimetric titration has been applied to two organic sulphur compounds, 2-mercapto-5-anilino-1,3,4-thiodiazol and hydrazine-*N*,*N'*-bisthiocarbonic acid allyl-monoamide, which are weakly acidic. A discontinuous manual technique has been used, and in the case of the allyl-monoamide a transformation from rectangular to oblique co-ordinates allows for the influence of secondary processes on the thermal effect of the process of neutralisation. From the experimental results the heats of neutralisation of the compounds with sodium hydroxide have also been calculated.

Zusammenfassung—Die enthalpimetrische Titration wurde auf zwei schwach saure organische Schwefelverbindungen, 2-Mercapto-5-anilino-1,3,4-thiodiazol und Hydrazin-*N*,*N'*-bisthiocarbonsäure-allyl monoamid, angewandt. Es wurde mit diskontinuierlichem Handbetrieb gearbeitet. Im Falle des Allylmonoamids wird dem Einfluß von Sekundärprozessen auf den thermischen Effekt der Neutralisation durch Übergang von rechtwinkligen auf schiefwinklige Koordinaten Rechnung getragen. Aus den Versuchsergebnissen wurden auch die Neutralisationswärmen der Verbindungen mit Natriumhydroxyd berechnet.

BIBLIOGRAPHIE

[1] P. M. Dean et O. O. Watts, *J. Amer. Chem. Soc.*, 1924, **46**, 855; 1925, **47**, 64.
C. Mayr et J. Fisch, *Z. analyt. Chem.*, 1929, **76**, 418.
[2] P. Dutoit et E. Grobet, *J. Chim. Phys.*, 1921, **19**, 324, 331.
[3] J. Jordan et T. G. Alleman, *Analyt. Chem.*, 1957, **29**, 9.
[4] H. W. Linde, L. B. Rogers et D. N. Hume, *ibid.*, 1953, **25**, 404.
[5] J. Jordan et M. P. Ben-Jair, *Ark. Kemi*, 1957, **11**, 25.
[6] P. Mondain-Monval et R. Paris, *Bull. Soc. Chim.* (3), 1938, **5**, 1641.
[7] C. Drăgulescu et S. Policec, *Studii si cercetări st. Chimice, Timisoara*, 1962, tom. IX, 1-2, 33.
[8] E. Popper, L. Popa, V. Junie et L. Roman, *Studii si cercetări de Chimie (Cluj)*, 1957, **3-4**, 269; *idem*, *Revista de chimie*, 1960, **11**, 1, 44-46.

Talanta 1964, Vol. 11, pp. 523 to 530. Pergamon Press Ltd. Printed in Northern Ireland

ANION-EXCHANGE BEHAVIOUR OF URANIUM AND OTHER ELEMENTS IN THE PRESENCE OF ALIPHATIC DI- AND TRICARBOXYLIC ACIDS

METHOD FOR THE SEPARATION OF URANIUM FROM THORIUM AND RARE EARTHS

J. Korkisch and I. Hazan
Analytical Institute of University of Vienna, IX Währingerstrasse 38, Austria

(*Received* 1 *August* 1963. *Accepted* 10 *October* 1963)

Summary—The exchange behaviour of uranium, thorium, the rare earths and some other elements towards the strongly basic anion exchanger Dowex 1 in aqueous and methanolic systems containing di- or tricarboxylic acids is described. Based on the measurement of the distribution coefficients in such media a method for the separation of uranium from thorium and the rare earths in an aqueous solution containing malonic acid has been developed.

INTRODUCTION

Investigations carried out by Zaki and Shakir[1] have shown that uranium can be separated from other elements on an anion exchanger by using buffered solutions of oxalic, succinic or adipic acid. Uranium, thorium and zirconium, as well as other elements, form with these acids negatively charged complexes which are strongly retained by the exchange resin.[1–3] Several other authors have also reported on the adsorption behaviour of uranium and various other elements from solutions containing organic acids, such as acetic[4–6] and ascorbic acid.[7–9]

Previous research work dealing with the anion-exchange behaviour of uranium and other elements in organic acid-organic solvent mixtures[10] showed that in such media many separation possibilities for uranium could be uncovered. For this reason we have now investigated the behaviour of some elements in the presence of polyfunctional organic acids, especially the homologous dicarboxylic acids of the aliphatic series.

EXPERIMENTAL

Reagents

Ion-exchange resin. The strongly basic anion exchanger Dowex 1, ×8 (100–200 mesh, chloride form) was used. For the equilibrium and separation experiments in the various media the corresponding organic acid forms of this resin were employed. The preparation of these forms was performed according to the directions previously given for the monocarboxylic acid forms.[10]

Standard solutions of uranium and other elements. Hydrochloric or nitric acid solutions of the chlorides or nitrates of precisely known element content were employed. For each experiment an aliquot corresponding to the desired amount of the element to be investigated was evaporated to dryness on a water bath. To the residue thus obtained, first the solid organic acid and then the solvent was added.

Organic acids and solvent. The following reagent-grade acids were employed: oxalic, malonic, succinic, glutaric, *d,l*-tartaric and citric. The methanol employed was also of reagent-grade purity.

Apparatus

The column operations were carried out in columns of the same type and dimensions as described earlier.[7] For the fluorimetric determination of uranium a Galvanek Morrison Mark V fluorimeter and for the spectrophotometric determination of the other elements a Beckman Model B spectrophotometer was employed.

Quantitative determination of elements investigated

The determination of uranium was performed fluorimetrically,[11] and that of thorium and the rare earths spectrophotometrically by employing the azo dye Solochromate Fast Red.[12,13] The other elements were determined quantitatively using photometric methods recommended by Sandell.[14]

Determination of distribution coefficients

The distribution coefficients of all elements were determined in the same manner as has earlier been described for the equilibrium experiments in mineral acid-organic solvent[15] and organic acid-organic solvent[10] mixtures. Twenty ml of solvent, containing a certain amount of the acid and 5 mg of the element in question, were equilibrated with 1 g of the resin. The results of the experiments shown in Figs. 1 and 2 were obtained by using varying amounts of acid whereas those recorded in Fig. 3 and in Table I were always performed in the presence of 1 g of acid.

Column operations

All separation experiments on resin columns were performed by employing the following working procedure.

Pretreatment of resin bed. In order to transform the chloride form of the resin into the malonate form the resin bed was treated with a 10% aqueous malonic acid solution which had been buffered to a pH of approximately 5 to 6 with aqueous ammonia. As soon as the effluent was free from chloride ions (which was usually the case after the passage of less than 50 ml of this solution), the resin was washed with 50 ml of a solution (washing solution) containing 50 g of malonic acid/1,000 ml of distilled water.

Adsorption of uranium. The sorption solution was prepared by dissolving the residue obtained by evaporation of certain amounts of the standard solutions of the elements in question, first by adding 5 g of malonic acid to the dry residue, followed by 100 ml of distilled water. This solution was passed through the column at a flow rate of 0·5–0·75 ml/min. During this operation uranium was strongly adsorbed whereas the other elements, *i.e.*, thorium, cerium and gadolinium, passed into the effluent.

Washing process. In order to remove the last traces of the other elements the resin bed was washed with 50 ml of the washing solution.

Elution. The uranium was eluted with 100 ml of 1M hydrochloric acid.

Further treatment of eluate and effluent. After evaporation of the eluate to dryness (water bath) the uranium was determined as previously described.[15] During this process as well as when evaporating the effluent, malonic acid was decarboxylated, whereby acetic acid was formed, so that very little organic matter was present in the residue. In the residues obtained after evaporation of the effluents, thorium and the rare earths were determined by previously described procedures.[12,13]

The results of a series of such column separations are recorded in Table II.

RESULTS

Effect of acid concentration on distribution coefficients of uranium and thorium

In Figs. 1 and 2 the results of the experiments performed in aqueous and methanolic solutions containing varying amounts of the organic acids are recorded.

Although the adsorption of uranium from oxalic acid solutions is higher than from all mixtures containing other acids, it did not seem practical to use this acid for further investigations because its solubility in water is rather low; furthermore, it forms insoluble precipitates with thorium, the rare earths and other elements in aqueous as well as in methanolic media. In malonic acid mixtures, however, both these adverse effects are not observed so that this acid was employed for the separation of uranium, thorium and rare earths on ion-exchange columns.

By comparing Fig. 1 with Fig. 2 it can clearly be seen that the difference existing between the adsorption of uranium in aqueous and methanolic solutions is rather large (especially at a higher acid concentration) in comparison with that of thorium, which shows in both solvents a practically identical adsorption behaviour. Besides,

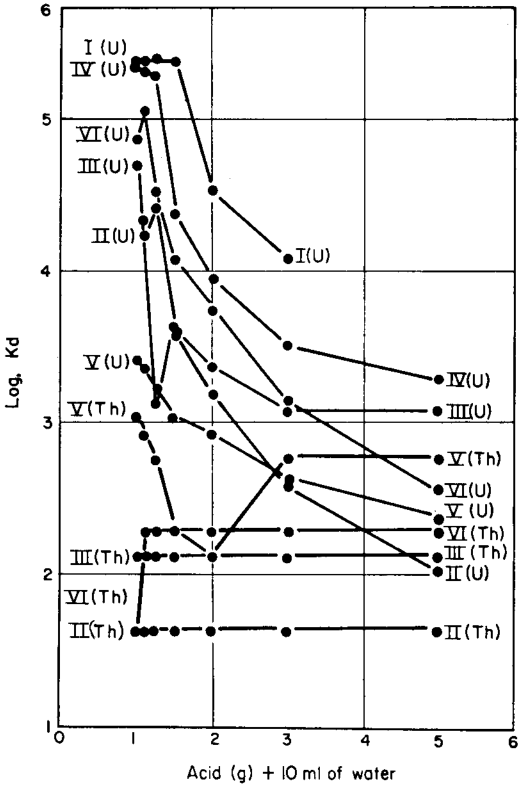


FIG. 1.—Adsorption of uranium and thorium from aqueous solutions containing di- and tricarboxylic acids:

I—oxalic acid,	IV—glutaric acid,
II—malonic acid,	V—tartaric acid,
III—succinic acid,	VI—citric acid.

its solubility in methanolic solutions is rather limited. That is why in Fig. 2 only two curves for thorium could be established. Several experiments in other solvents, *e.g.*, ethanol, n-propanol, acetone, *etc.*, with some of the acids have shown that the adsorption of uranium from tartaric and citric acid media did not deviate appreciably from the results obtained in methanolic solutions, whereas in the presence of the other acids a decrease of uranium adsorption with increasing chain length of the alcohols could be observed[15] in the case of oxalic acid. Because of the low solubility of the acids, however, no systematic investigations as to the adsorption of uranium or other elements were conducted in solvents other than water and methanol.

Effect of water-methanol concentration

In Fig. 3 the variation of the distribution coefficients of uranium at different water to methanol ratios is shown. From the results it is seen that the Kd of uranium in the dicarboxylic acid-methanol-water mixtures does not vary as much with increasing percentage of methanol as in tartaric and citric acid media, where a sharp decline of the Kd occurs when increasing the methanol content of the mixtures from 80 to 100%. This is because the hydrophilic hydroxyl groups of these acids gradually lose their complex-forming tendencies by a decrease in the water content of the mixtures. In

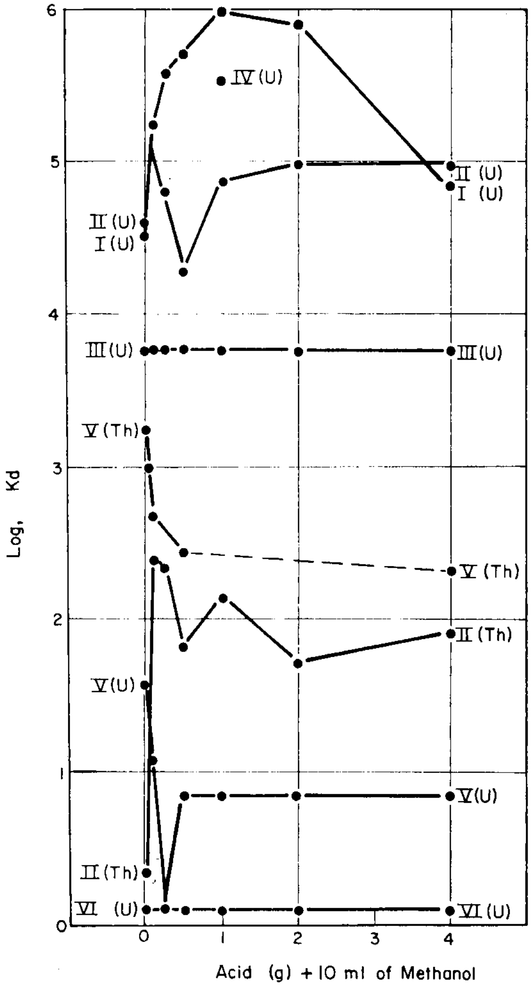


FIG. 2.—Adsorption of uranium and thorium from methanolic solutions containing di- and tricarboxylic acids:
I—oxalic acid, IV—glutamic acid,
II—malonic acid, V—tartaric acid,
III—succinic acid, VI—citric acid,
- - - - region of insolubility.

the case of the dicarboxylic acids without hydroxyl groups, however, the adsorption of uranium in 100% aqueous solutions of the acids is less than in 100% methanol solutions of the acids, so that in the presence of these acids an increase of the methanol concentration increases the uranium adsorption.

Adsorption behaviour of other elements

In Table I the distribution coefficients of a series of other elements in aqueous and methanolic media containing malonic, succinic, glutaric, tartaric and citric acid are recorded.

For comparison purposes the distribution coefficients of uranium and thorium in the various media have also been included in this table.

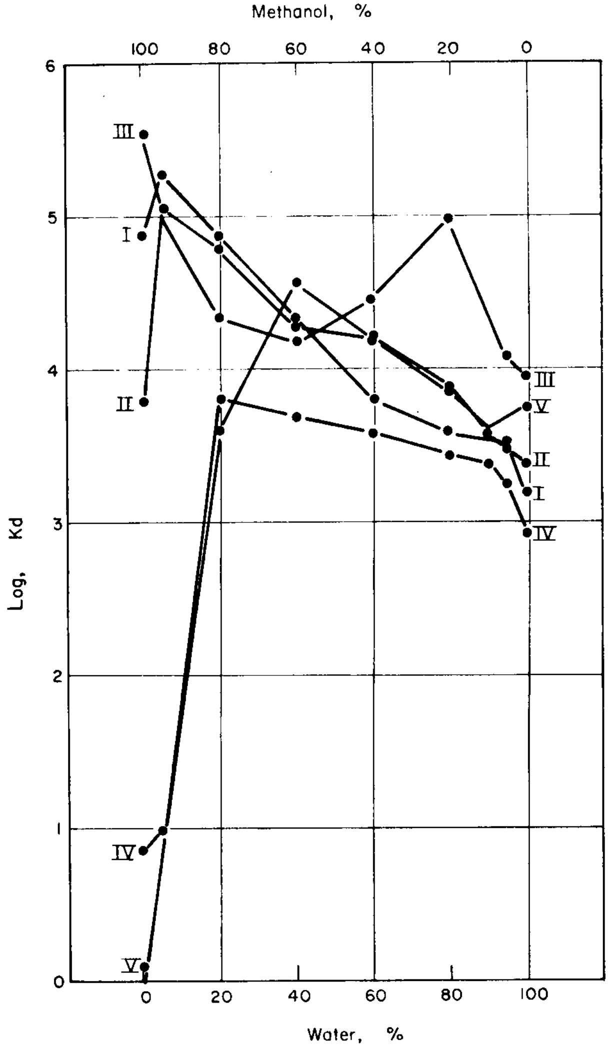


FIG. 3.—Effect of water-methanol concentration on uranium adsorption:
I—malonic acid, III—glutaric acid,
II—succinic acid, IV—tartaric acid,
V—citric acid.

From the results it is seen that malonic acid in methanol is superior to the other di- and tricarboxylic acids in-so-far as it shows the greatest solubility and sufficient acid strength to keep most of the investigated elements in solution without forming precipitates or causing hydrolysis. In aqueous solutions, however, all of the acids can be employed for the adsorption of uranium with nearly equal effect, irrespective of their chemical constitution. For the purpose of separating uranium from thorium and other elements (with the exception of iron, which could easily be separated from uranium in a water-succinic acid medium), the use of malonic acid seemed to be advantageous because most of the elements, except for iron and yttrium, show rather low distribution coefficients in aqueous malonic acid solutions.

TABLE I.—DISTRIBUTION COEFFICIENTS OF VARIOUS ELEMENTS

Element	Acid	Solvent	
		Water	Methanol
UO_2^{2+}	Malonic acid	1,540	77,000
Th^{4+}	Malonic acid	45	142
La^{3+}	Malonic acid	12	240
Ce^{3+}	Malonic acid	33	1,470
Pr^{3+}	Malonic acid	1·0	×
Nd^{3+}	Malonic acid	1·0	270
Sm^{3+}	Malonic acid	0·1	670
Eu^{3+}	Malonic acid	0·1	708
Gd^{3+}	Malonic acid	1·0	885
Tb^{3+}	Malonic acid	1·0	690
Dy^{3+}	Malonic acid	8·0	800
Ho^{3+}	Malonic acid	0·1	465
Er^{3+}	Malonic acid	1·0	550
Tm^{3+}	Malonic acid	1·0	505
Yb^{3+}	Malonic acid	1·0	650
Lu^{3+}	Malonic acid	1·0	670
Sc^{3+}	Malonic acid	100	×
Mg^{2+}	Malonic acid	1·0	8·0
Ca^{2+}	Malonic acid	0·5	×
Sr^{2+}	Malonic acid	10·0	10·0
Zn^{2+}	Malonic acid	1·0	170
Cd^{2+}	Malonic acid	1·0	15
Al^{3+}	Malonic acid	1·0	16,660
In^{3+}	Malonic acid	1·0	1,920
Cu^{2+}	Malonic acid	6·3	435
Pb^{2+}	Malonic acid	0·1	×
Bi^{3+}	Malonic acid	33·5	490
Mn^{2+}	Malonic acid	1·0	×
Fe^{3+}	Malonic acid	324	×
Co^{2+}	Malonic acid	0·1	0·1
Ni^{2+}	Malonic acid	3·2	12·0
UO_2^{2+}	Succinic acid	2,400	6,000
Th^{4+}	Succinic acid	84	×
Ce^{3+}	Succinic acid	×	×
Gd^{3+}	Succinic acid	40	×
Cu^{2+}	Succinic acid	7·0	×
Bi^{3+}	Succinic acid	65·0	×
Fe^{3+}	Succinic acid	1·0	×
Co^{2+}	Succinic acid	0·1	0·1
Ni^{2+}	Succinic acid	6·6	6·6
UO_2^{2+}	Glutaric acid	9,500	340,000
Pb^{2+}	Glutaric acid	0·1	×
Bi^{3+}	Glutaric acid	107	×
UO_2^{2+}	Tartaric acid	1,000	7·0
Th^{4+}	Tartaric acid	147	×
Ce^{3+}	Tartaric acid	40	×
Cu^{2+}	Tartaric acid	7·0	×
Bi^{3+}	Tartaric acid	507	×
Fe^{3+}	Tartaric acid	160	×
Co^{2+}	Tartaric acid	0·1	0·1
Ni^{2+}	Tartaric acid	17·2	6·6
UO_2^{2+}	Citric acid	5,900	1·0
Th^{4+}	Citric acid	200	×

TABLE I (*Continued*)

Element	Acid	Solvent	
		Water	Methanol
Ce^{3+}	Citric acid	11·5	×
Gd^{3+}	Citric acid	815	×
Cu^{2+}	Citric acid	48·5	×
Bi^{3+}	Citric acid	×	×
Fe^{3+}	Citric acid	203	×
Co^{2+}	Citric acid	0·1	0·1
Ni^{2+}	Citric acid	1·0	1·0

× In these media completely or partially insoluble.

In methanolic solutions of this acid, on the other hand, the possibility of co-adsorbing uranium together with thorium, the rare earths and other elements exists, so that malonic acid can be regarded as a more versatile complexing agent than the other acids, the element salts of which are also poorly soluble in methanol.

Separation procedure

Based on the results presented in Figs. 1 and 2 and in Table I a method of separating uranium from thorium, cerium and gadolinium (as representatives of the rare earth elements) in an aqueous medium was developed. The experimental steps involved in this ion-exchange procedure have been described above under *Column operations.*

In Table II the results of these resin column separations are recorded. It is seen that all separations of uranium from the other elements were practically quantitative. For this reason and because the break-through capacity for uranium under these conditions (2g of resin in column 15 cm high and 0·5 cm diameter) was found to be

TABLE II.—SEPARATION OF URANIUM FROM OTHER ELEMENTS IN AQUEOUS MALONIC ACID MIXTURES*

Uranium taken, μg	Element to be separated from uranium, μg	Uranium recovered, μg	Other element recovered, μg
10,000	Th: 5,000	9,950	4,960
5,000	Th: 1,000	4,975	985
5,000	Th: 100	4,937	100
5,000	Th: 50	4,950	48
5,000	Th: 20	5,010	21
10,000	Ce: 500	9,980	492
5,000	Ce: 100	4,978	95·8
5,000	Ce: 50	4,967	50
5,000	Ce: 25	5,000	24
5,000	Ce: 10	4,986	9·5
10,000	Gd: 500	10,013	497
5,000	Gd: 100	5,000	97
5,000	Gd: 50	4,980	48
5,000	Gd: 25	4,978	27
5,000	Gd: 10	5,000	11

* Each result is the average of 3 separations performed under the same experimental conditions.

60 mg of uranium, this procedure could be employed effectively for the removal of fission products like the rare earths, strontium, *etc.*, from uranium.

By this anion-exchange method not only the separation of these elements from uranium can be accomplished but also from a series of other elements (those having sufficiently low distribution coefficients, *viz.* <50). It is, therefore, of broad applicability, unlike the method described by Zaki and Shakir[1] which has only limited use for analytical purposes.

Acknowledgements—This research was sponsored by the International Atomic Energy Agency and the United States Atomic Energy Commission under Contract No. 67/US (AT(30-1)-2623). The generous support from these agencies is gratefully acknowledged.

Zusammenfassung—Es wurde das Ionenaustauschverhalten von Uran, Thorium, der seltenen Erden und einiger anderer Elemente gegenüber dem stark basischen Anionenaustauscher Dowex 1 in wäßrigen und methanolischen Systemen die Di- oder Tricarboxylsäuren enthalten untersucht. Auf Grund von Messungen der Verteilungskoeffizienten in derartigen Medien konnte eine Methode zur Trennung des Urans von Thorium und den seltenen Erden in malonsaurer wäßriger Lösung entwickelt werden.

Résumé—On décrit l'échange de l'uranium, du thorium, des éléments de terres rares et de quelques autres éléments en présence de l'échangeur d'anions fortement basique Dowex 1 dans des systémes aqueux ou méthanoliques contenant des acides di- ou tricarboxyliques. Développement d'une méthode basée sur la mesure des coefficients de distribution dans de tels milieux, pour séparer l'uranium du thorium et des éléments des terres rares en solution aqueuse contenant de l'acide malonique.

REFERENCES

[1] M. R. Zaki and K. Shakir, *Z. Analyt. Chem.*, 1962, **185**, 423.
[2] *Idem, ibid.*, 1961, **180**, 188.
[3] H. Khalifa and M. R. Zaki, *ibid.*, 1957, **158**, 1.
[4] F. Hecht, J. Korkisch, R. Patzak and A. Thiard, *Mikrochim. Acta*, 1956, 1283.
[5] J. Korkisch, A. Thiard and F. Hecht, *ibid.*, 1956, 1422.
[6] J. P. Riley and H. P. Williams, *ibid.*, 1959, 825.
[7] J. Korkisch, A. Farag and F. Hecht, *ibid.*, 1958, 415.
[8] J. Korkisch, P. Antal and F. Hecht, *ibid.*, 1959, 693.
[9] J. Korkisch and F. Tera, *Analyt. Chem.*, 1961, **33**, 1265.
[10] J. Korkisch, Report to International Atomic Energy Agency and U.S. Atomic Energy Commission under contract No 67/US(AT(30–1)–2623). September 1963.
[11] T. Schönfeld, M. El Garhy, C. Friedmann and J. Veselsky, *Mikrochim. Acta*, 1960, 883.
[12] J. Korkisch and G. E. Janauer, *Analyt. Chem.*, 1961, **33**, 1930.
[13] J. Korkisch, I. Hazan and G. Arrhenius, *Talanta*, 1963, **10**, 865.
[14] E. B. Sandell, *Colorimetric Determination of Traces of Metals.* Interscience Publ. Inc., New York, 3rd Ed., 1959.
[15] J. Korkisch and G. E. Janauer, *Talanta*, 1962, **9**, 957.

Talanta, 1964, Vol. 11, pp. 531 to 542. Pergamon Press Ltd. Printed in Northern Ireland

CHEMICAL COMPOUNDS FORMED IN THE COPRECIPITATION OF CATIONS WITH SULPHIDES

N. A. RUDNEV and G. I. MALOFEYEVA
Vernadsky Institute of Geochemistry and Analytical Chemistry,
Moscow, U.S.S.R.

(*Received* 8 *August* 1963. *Accepted* 11 *October* 1963)

Summary—A study of the coprecipitation of thallium with As_2S_3, SnS_2, MoS_3, Re_2S_7, PtS_2, PdS, Ru_2S_3, Rh_2S_3, Ir_2S_3 and In_2S_3, and of indium with CuS and Ag_2S by physicochemical analysis has shown that the process results from formation of the following compounds: $TlAsS_2$, $TlSnS_2$, $TlMoS_2$, $TlReS_4$, $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$, $TlRh_2S_4$, Tl_3Ir_3S, $TlIn_2S_3$, $CuInS_2$ and $AgInS_2$. A type of coprecipitation diagram characteristic for the case of the formation of chemical compounds has been established and the fields on it, corresponding to phases of definite composition, have been delimited. The formation in the coprecipitation of microdisperse systems of "colloidal" solid solutions of one sulphide in another has been shown.

VARIOUS views have been put forward to explain the reasons for the coprecipitation of cations with sulphides.[1,2] A number of authors consider that the entrainment of cations by sulphides results from formation of chemical compounds. Feigl explains the coprecipitation by the formation of heteropolymers or mixed sulphides of the type: $Me^{I}S\text{–}SMe^{II}$.[3–5] Okač also indicates the formation of heteropolysulphides $(MeS)_x\ (Me'S)_y$.[6] He states that x and y may in special cases correspond to the stoichiometric figures for hypothetical complex compounds of the general formula $[Me(SMe')_x]S$. According to Hawley's results, in the simultaneous precipitation of Tl_2S and SnS_2 and also of Tl_2S and As_2S_5, compounds of the composition Tl_4SnS_4 and Tl_3AsS_4 are formed.[7,8] Bruner and Zawadzki mention the compound $Tl_2S{\cdot}4CuS$, which, in their opinion, is obtained in the coprecipitation of thallium with CuS.[9] Malfatti considers that the precipitation of FeS in the presence of the alkali and the alkaline-earth metals gives thiosalts of the composition $MeFeS_2$ and $Me(FeS_2)_2$, where Me is a uni- or bivalent cation.[10] The compounds $PbS{\cdot}Tl_2S$ and $GaS{\cdot}ZnS$, formed in the coprecipitation of thallium with PbS and of gallium with ZnS, respectively, are referred to by Nanobashvili *et al.*[11,12] In the precipitation of sulphides of copper and germanium, Davydov and Diyev obtained a precipitate with a composition close to that for the compound $CuS{\cdot}GeS_2$.[13]

In the papers discussed, only individual facts indicating the formation of chemical compounds under certain conditions are given. In the majority of them, however, only hypotheses, not confirmed by direct experiments, are put forward about their formation. No investigations exist with a general approach to the solution of the question of the possibility of the formation of chemical compounds in coprecipitation.

In an investigation of the coprecipitation of thallium and indium with sulphides of the second analytical group of the classical hydrogen sulphide scheme, we found that the phenomenon was clearly expressed where the sulphides in the system possessed opposite—basic and acidic—properties. This fact gave grounds for assuming the formation of chemical compounds. Consequently, we considered it desirable to carry out investigations of the coprecipitation of cations with sulphides starting from the positions of the elements in the Periodic Table. This study of the phenomenon was carried out on the basis of physicochemical analysis.

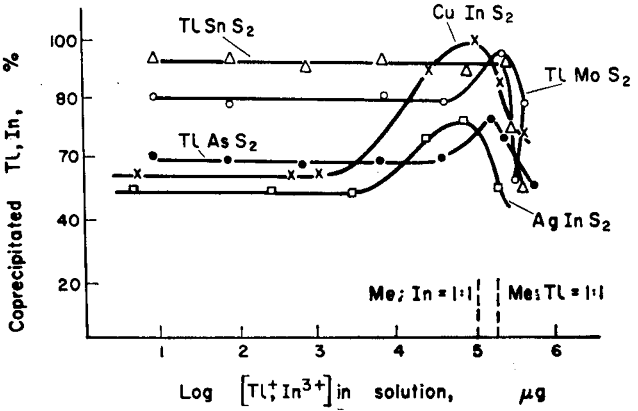


Fig. 1.—Coprecipitation diagrams of Tl with As_2S_3, SnS_2 and MoS_3, and of In with Ag_2S and CuS.

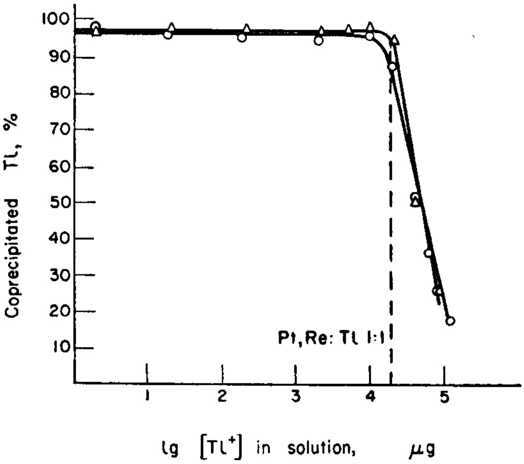


Fig. 2.—Coprecipitation diagrams of Tl with Re_2S_7 and PtS_2.

Physicochemical analysis with a constant concentration of one component and a variable concentration of the other was used. Construction of the coprecipitation diagrams was carried out by plotting as ordinates the amount of coprecipitation in per cent and as abscissae the logarithm of the concentration of the thallium or indium in the solution. The amount of coprecipitation was determined by a radioactive tracer method using the radioisotopes ^{204}Tl and ^{114}In.

EXPERIMENTAL

I. *Application of physicochemical analysis to the coprecipitation of thallium and indium with sulphide*

Below we give data on the coprecipitation in a series of systems for sulphides of the metals mentioned.

The systems Tl^+, H^+/AsO_3^{3-}, S^{2-}; Tl^+, H^+, Sn^{4+}/S^{2-}; Tl^+, H^+/MoO_4^{2-}, S^{2-}; and Tl^+, H^+/ReO_4^-, S^{2-}. From the breaks in the coprecipitation diagrams given in Figs. 1 and 2 may be deduced the formation of compounds having ratios of As, Sn, Mo and Re to Tl of 1:1.

The constancy of the distribution coefficient of thallium in the case of the coprecipitation of small concentrations of thallium is striking.*

Analysis of the compounds isolated showed that they had the following compositions: $TlSnS_2$, $TlAsS_2$, $TlMoS_3$ and $TlReS_4$.

An X-ray examination of Tl_2S, As_2S_3, SnS_2, MoS_3 and Re_2S_7, and also of $TlSnS_2$, $TlAsS_2$, $TlMoS_3$ and $TlReS_4$, gave amorphous pictures.

The systems Cu^{2+}, In^{3+}, H^+/S^{2-}; Ag^+, In^{3+}, H^+/S^{2-}. As follows from the coprecipitation diagrams given (Fig. 1), chemical compounds are also formed in these systems. The breaks in the diagrams correspond to a ratio in the precipitates of Cu or Ag to In of 1:1.

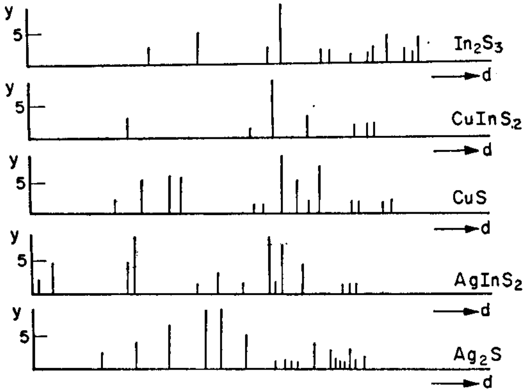


FIG. 3.—Results of calculation of the X-ray diagrams for CuS, In_2S_3, $CuInS_2$, Ag_2S and $AgInS_2$.

The behaviour of low concentrations of indium is analogous to the cases of the coprecipitation of thallium already considered.

From the results of analysis, the compositions of these compounds are as follows: $CuInS_2$ and $AgInS_2$.

X-ray investigation showed diffraction pictures for $CuInS_2$ and $AgInS_2$ different from those for the starting materials CuS, Ag_2S and In_2S_3, which is characteristic for the formation of chemical compounds (Fig. 3).

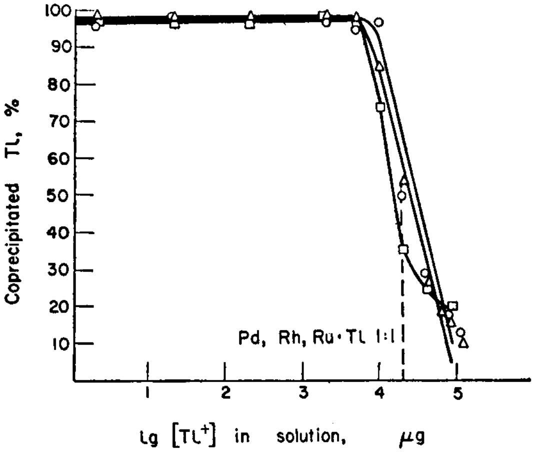


FIG. 4.—Coprecipitation diagrams of Tl with Rh_2S_3, Ru_2S_3 and PdS.

---

* The distribution coefficient may be calculated from the formula $K = \frac{C_{\text{solid phase}}}{C_{\text{solution}}}$

The systems Tl^+, H^+/Pt^{IV}, S^{2-}; Tl^+, H^+/Pd^{II}, S^{2-}; Tl^+, $H^+/Ru,^{III}$ S^{2-}; *and* Tl^+, H^+/Rh^{II}, S^{2-} Analogous results were also obtained in the coprecipitation of thallium with sulphides of the platinum metals. As can be seen from the diagrams given (Fig. 4), in contrast to those obtained previously the breaks in the curves correspond to a ratio of Pd, Ru and Rh to Tl of 2:1. In the case of the coprecipitation of Tl with PtS_2, the ratio of Tl and Pt in the compound formed is 1:1 (Fig. 2).

Analysis of the compounds obtained showed that they had the compositions: $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$ and $TlRh_2S_4$. The results of calculation of the X-ray diagrams for $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$ and $TlRh_2S_4$ are given in Fig. 5. For PtS_2, PdS, Ru_2S_3 and Rh_2S_3, amorphous X-ray pictures were obtained.

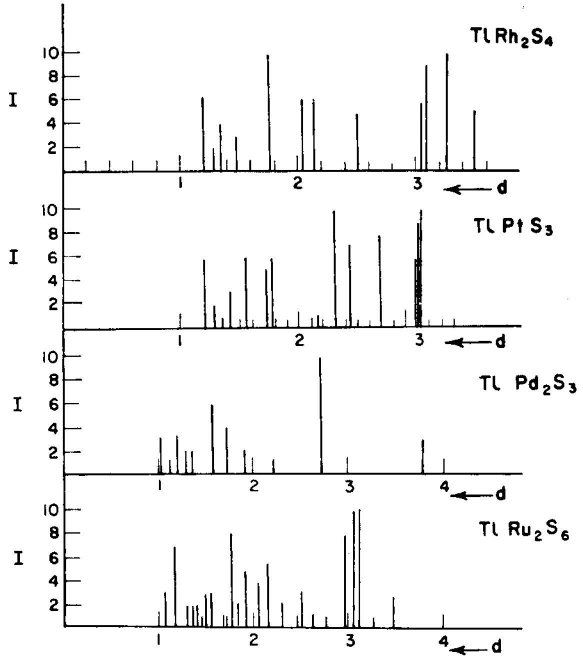


FIG. 5.—Results of the calculation of the X-ray diagrams for $TlRh_2S_4$, $TlPtS_3$, $TlPd_2S_3$ and $TlRu_2S_6$.

The systems Tl^+, H^+/Ir^{III}, S^{2-}; In^{3+}, Tl^+, H^+/S^{2-}. In a study of the coprecipitation of thallium with Ir_2S_3, a diagram somewhat different from those given above was obtained (Fig. 6). From the break in the curve, as in the diagrams given in Figs. 1, 2 and 4, it may be concluded that a compound with a Tl:Ir ratio of 1:1 is formed.

Analysis of the compound formed showed that it had the composition Tl_3Ir_3S, the unusual nature of which is striking.

The most interesting field in the diagram obtained is C, characterising a proportionality between the concentration of the cation in the solution and in the solid phase, which shows the formation of solid solutions (the distribution coefficient may be calculated from the formula $K = \frac{C_{\text{solid phase}}}{C_{\text{solution}}}$

The X-ray diagrams of Tl_3Ir_3S and Ir_2S_3 are given in Fig. 7. The difference in the position and intensity of the lines of the Tl_3Ir_3S X-ray diagram as compared with that for Ir_2S_3 confirms the formation of a chemical compound.

It follows from the results of our study of coprecipitation in the systems given above that the formation of chemical compounds is found in those cases where one of the sulphides of the given system possesses basic properties and the other acidic properties. The elements giving these compounds are located in different groups of the Periodic Table. The rule mentioned has been confirmed in many cases of the coprecipitation of thallium with sulphides of an acidic character and of indium with sulphides of a basic character. It is quite natural to assume that the coprecipitation of thallium with In_2S_3 will also lead to the formation of a chemical compound. The results obtained are given in Fig. 8. The break in the diagram corresponds to an In:Tl ratio in the precipitate of 1:0·5.

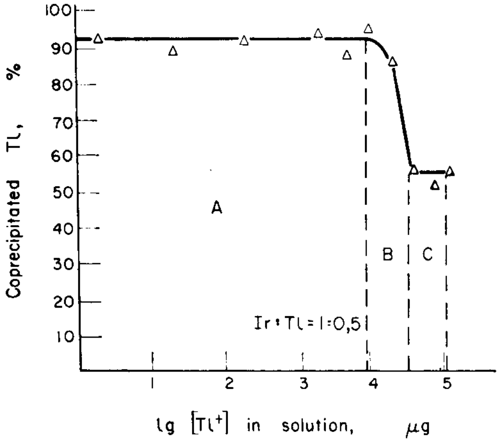


FIG. 6.—Coprecipitation diagram of Tl with Ir_2S_3.

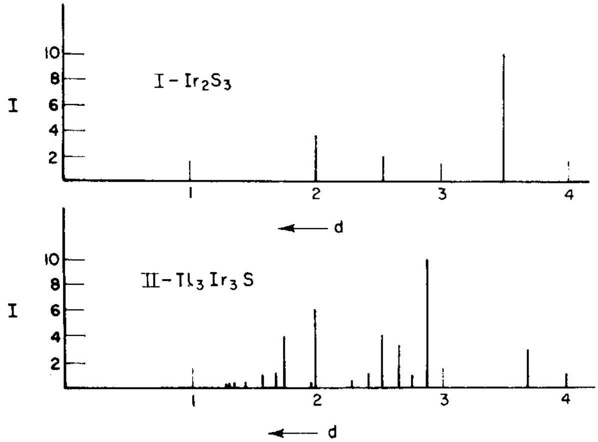


FIG. 7.—Results of the calculation of the X-ray diagrams for Tl_3Ir_3S and Ir_2S_3.

Of particular interest is the shape of the curve for ratios of In to Tl in the solution of 1:10, 1:12, 1:14 and 1:16, where there is a constant degree of coprecipitation of thallium with In_2S_3. On the diagram, this corresponds to the parallel course of the coprecipitation curve. The constancy of the distribution of thallium between the solution and the solid phase shows the formation of a solid solution of this composition with an excess of Tl_2S (field D).

Analysis of the precipitate showed that the compound obtained had the composition $TlIn_2S_3$. The X-ray diagrams of $TlIn_2S_3$ and In_2S_3 are given in Fig. 9. The difference in the position and intensity of the lines of the X-ray diagrams of $TlIn_2S_3$ and In_2S_3 is characteristic for a chemical compound.

Thus, in spite of the presence of indium and thallium in a single Sub-Group of the Periodic Table, in consequence of which the acidic—basic properties of In_2S_3 and Tl_2S differ less than for the sulphides of the elements mentioned above, the formation of a chemical compound also takes place in this case.

II. *X-ray investigation of the solid phases obtained in coprecipitation when a chemical compound is formed*

A more complete idea of the reactions in the solid phases for the investigated concentrations of the coprecipitating cation can be obtained by the use of X-ray analysis.

In the majority of the systems which we studied, the sulphides were amorphous to X-rays, which limited their application. The system Cu^{2+}, In^{3+}, H^+/S^{2-} proved to be suitable, because CuS, In_2S_3 and $CuInS_2$ give sharp X-ray diagrams.

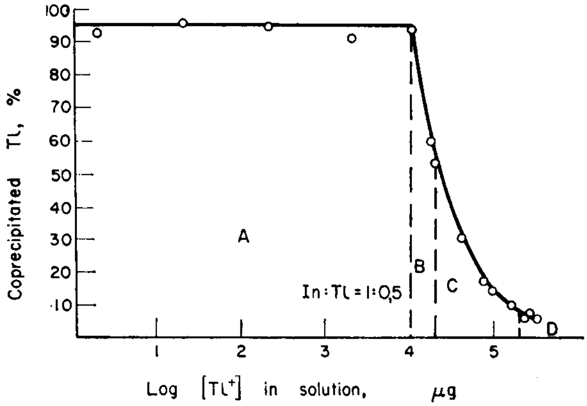


FIG. 8.—Coprecipitation diagram for Tl with In_2S_3.

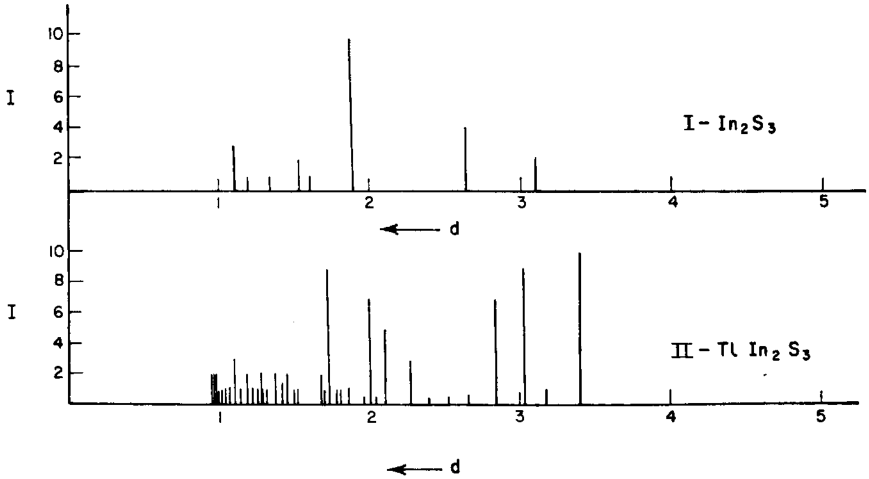


FIG. 9.—Results of the calculation of the X-ray diagrams of In_2S_3 and $TlIn_2S_3$.

The diagrams of coprecipitation of indium with CuS are given in Fig. 10.

The changes in the composition of the phases formed in the coprecipitation of various concentrations of In^{3+} with CuS are shown schematically in Fig. 11 on the basis of the results of the X-ray analysis.

In this diagram (Fig. 11) there are three regions: a single-phase region A′ (the pure CuS component), a two-phase region A (CuS + $CuInS_2$ in various proportions) and a single-phase region ($CuInS_2$).

Field A, where there is a constant distribution of indium between the solution and the solid phase, indicates the formation of solid solutions. However, it follows from the X-ray diagrams that this is a two-phase region. This contradiction can be resolved by assuming in our case the formation of a microdisperse system where the dispersion medium is CuS and the dispersed substance is $CuInS_2$. The structure, the particle size and the features of its formation are such that the uniform distribution of one phase in the other is possible. As can be seen from Fig. 11, from a certain ratio between CuS and $CuInS_2$ onwards, the latter will be the dispersion medium and the CuS will be the dispersoid.

The following facts favour this hypothesis. In the case of the coprecipitation of In^{3+} with CuS, because its molecules are being formed at the moment when the CuS produced passes through the colloidal stage, a uniform distribution of the compound formed, $CuInS_2$, throughout the volume of the CuS gel is quite natural. Entrainment of indium after the separation of the CuS in the form of a solid phase must also give a uniform distribution of $CuInS_2$ by virtue of the extremely high porosity of CuS and the possibility of the interaction of the In^{3+} ion practically throughout the mass of CuS, The exceptionally large specific surface of sulphide precipitates (600 m^2) follows from its determination

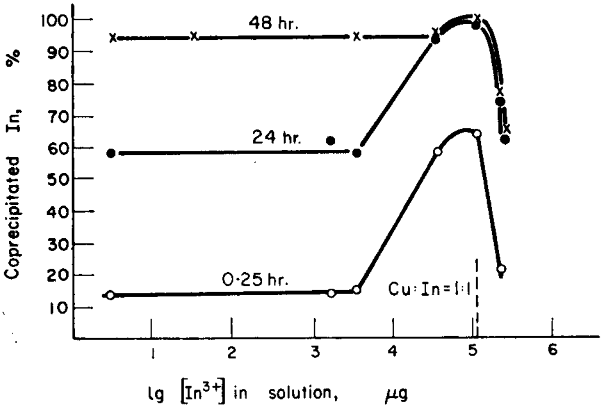


Fig. 10.—Coprecipitation diagram of In with CuS.

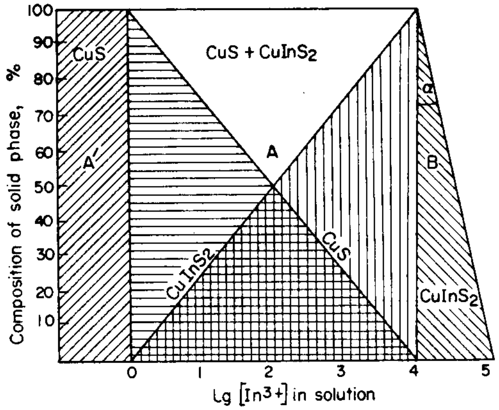


Fig. 11.—Change in the composition of the phases obtained in the coprecipitation of various concentrations of In^{3+} with CuS.

by the sorption of surface-active dyes[14] and by isotopic exchange between ions in the solution and the solid sulphide phase,[15] and also from electron-microscope pictures.[14,16]

The X-ray diagrams of the precipitates recorded were used to determine the particle dimensions of the phases of interest to us. Calculations of the mean effective grain size were carried out by Selyakov's formula.[17]

As the results showed, the mean effective grain size for CuS and $CuInS_2$ was *ca.* 3×10^{-6} cm. Consequently, the particles of $CuInS_2$, with a degree of dispersion of 3×10^{-6} cm, are distributed in a precipitate of CuS with a particle size of the same order.

According to the hypothesis being discussed, the constancy of the distribution coefficient is connected with the formation of solid solutions with a molecular degree of dispersion of the components. The results we obtained indicate the possibility of the compatibility of the constancy of the distribution of the coprecipitated cation and the absence of a molecularly dispersed distribution of one component in the other. In the present case, we encounter new facts requiring a revision of the hypotheses that have become established.

III. *Conditions of formation and properties of the compounds*

The compounds concerned are obtained as the result of coprecipitation, *i.e.*, under somewhat unusual conditions. Consequently, it was of interest to study these conditions and also the properties of the compounds arising. It is possible in this way to obtain a more profound insight into the coprecipitation process.

In view of the fact that the sulphide precipitates have an enormous surface with HS^- and S^{2-} ions present on it and giving to it a negative charge, it was essential to elucidate the role of adsorption in the formation of the compounds we were studying.

It was possible to elucidate the dependence of the coprecipitation on adsorption by studying the influence on the degree of coprecipitation of the conditions existing when the coprecipitating cation was added to a precipitate of previously separated sulphide and also when foreign ions were present in the solution.

The results obtained are given in Tables I and II.

TABLE I—COPRECIPITATION OF THALLIUM WITH Re_2S_7, PtS_2, PdS, Ru_2S_3 AND Ir_2S_3 UNDER VARIOUS CONDITIONS

	Coprecipitation of thallium, %			
		Addition to previously formed precipitate		
Metal sulphide	At the moment of formation of the precipitate	Unwashed	Washed with H_2O	Washed with H_2O, but on the addition of Tl H_2S–H_2O was introduced
Re_2S_7	51·7	40·7	6·5	15·8
PtS_2	49·9	21·6	2·6	10·1
PdS	49·6	37·9	7·9	16·4
Ru_2S_3	49·5	50·9	6·1	25·5
Ir_2S_3	56·7	24·2	1·6	—

TABLE II—INFLUENCE OF FOREIGN IONS ON THE COPRECIPITATION OF THALLIUM WITH Re_2S_7, PtS_2, PdS AND Ru_2S_3

	Coprecipitation of thallium, %			
Foreign electrolyte	For a Re:Tl ratio in the solution of 1:2	For a Pd:Tl ratio in the solution of 1:1	For a Ru:Tl ratio in the solution of 1:1	For a Pt:Tl ratio in the solution of 1:2
$MgSO_4$(4·9 mg of Mg)	54·2	51·1	50·1	52·8
$Al_2(SO_4)_3$(5·4 mg of Al)	52·4	48·8	50·9	49·1
$ZnSO_4$(6·5 mg of Zn)	50·1	50·0	51·2	51·9
In the absence of foreign electrolyte	51·7	49·6	49·5	49·9

As the results given show, the coprecipitation of thallium at the moment of formation of Ru_2S_3 is identical with that produced by a previously formed precipitate of this sulphide. In the case of Re_2S_7, PtS_2, PdS and Ir_2S_3, thallium is coprecipitated in considerably greater amount than when it is added to preformed precipitates of these sulphides. Precipitates of sulphides first washed free from H_2S with water entrain thallium to only a slight extent. However, if a washed sulphide is added to a sulphuric acid solution containing H_2S, then marked coprecipitation of the thallium is again found.

The presence of large amounts of foreign cations—Mg^{2+}, Al^{3+}, Zn^{2+}—does not affect the degree of coprecipitation of the thallium with Re_2S_7, PtS_2, Ru_2S_3 and PdS. It follows from this that the formation of these compounds is not associated with an ordinary adsorption process. In order to obtain a more detailed explanation of the role of hydrogen sulphide in the process under study, the sorption by PdS of H_2S in solution in different concentrations was determined. Experiments were carried out at the same time with Ag_2S. The latter coprecipitates the cations from all sulphides to the smallest extent. Consequently, we desired to establish whether there was a relationship between the amounts of sorbed H_2S and the degree of coprecipitation of thallium.

The experiments showed that PdS and Ag_2S sorb approximately the same amounts of H_2S. Nevertheless, thallium is not coprecipitated with Ag_2S, or else this phenomenon is not exhibited to an appreciable extent.

The precipitates previously washed free from H_2S with water also entrain thallium to an inconsiderable extent.

Consequently, we may conclude that the presence of H_2S on the surface of the sulphides is a necessary, but not sufficient, condition for coprecipitation of the cations.

The chemistry of the phenomenon is also confirmed by the maintenance of stoichiometric ratios between the elements in the precipitate on the partial separation of the main component.

The results obtained are given in Table III.

TABLE III—COPRECIPITATION OF THALLIUM WITH PARTIAL SEPARATION OF Re_2S_7

Re precipitated, %	Tl coprecipitated, %	Ratio of Re to Tl in the precipitate
100	52·4	1:1·04
75·0	37·0	1:0·96
50·0	24·2	1:0·97
25·0	10·0	1:0·80

As follows from the results given, the amount of thallium is equivalent to the Re_2S_7 which separated, which is characteristic for the formation of chemical compounds.

It was also of interest to determine the solubility of the compounds obtained. These compounds were obtained by coprecipitation, *i.e.*, by a somewhat unusual method. Nevertheless, a determination of their solubilities was important from the point of view of using these compounds for analytical purposes.

Solubility figures determined from the contents in aqueous solutions of the given compounds of the ions Tl, Ag and Cu, respectively, are given in Table IV.

TABLE IV—SOLUBILITY OF THE COMPOUNDS OBTAINED IN WATER AT $t° = 25 \pm 0·5$

Compound	Solubility, *mole/litre*
$TlReS_4$	$7·3 \times 10^{-5}$
$TlPd_2S_3$	$2·0 \times 10^{-5}$
$TlRu_2S_6$	$3·4 \times 10^{-5}$
$TlPtS_3$	$4·4 \times 10^{-5}$
Tl_3Ir_3S	$4·9 \times 10^{-5}$
$TlRh_2S_4$	$0·49 \times 10^{-5}$
$TlAsS_2$	$4·5 \times 10^{-6}$
$TlMoS_2$	$2·5 \times 10^{-5}$
$TlSnS_2$	$2·2 \times 10^{-5}$
$AgInS_2$	$4·7 \times 10^{-9}$
$CuInS_2$	$6·3 \times 10^{-8}$

The figures in Table IV clearly show that the magnitude of the solubility is not characteristic for the sulphides. Moreover, magnitudes of the same order are obtained for all of the compounds.

The experiments on the addition of thallium to a previously separated precipitate of Ru_2S_3 proved to be extremely fundamental. Under these conditions, thallium is entrained in the same amounts as at the moment of separation of the Ru_2S_3. Consequently, it was necessary to determine whether the compound $TlRu_2S_6$ is formed by the reaction of the Tl^+ ion with Ru_2S_3 or whether the thallium is present on the surface of the Ru_2S_3 in the form of Tl_2S. The identical X-ray diagrams for these compounds show that the first hypothesis is correct.

DISCUSSION

The experimental results presented show that chemical compounds are very important in the sulphide coprecipitation process. For the formation of chemical compounds to take place in the coprecipitation process, the presence in the sulphides of opposing properties—acidic and basic—is necessary. This condition is connected with the position of the elements forming the sulphides in the Periodic Table. Consequently, knowing the components of a given system, it is possible to predict the formation of chemical compounds and, consequently, the degree of coprecipitation, its course and the properties of the solid phase formed.

In the case of the formation of chemical compounds, the coprecipitation diagrams obtained are of a single type; the difference between them consists only in the position of the breaks corresponding to the ratio of the components in the solid phase.

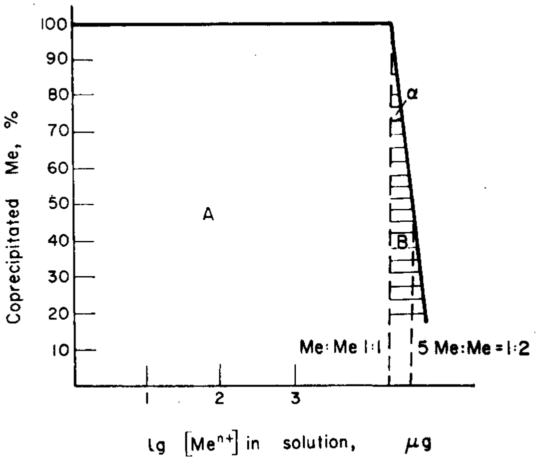


FIG. 12.—Theoretical coprecipitation diagram caused by formation of a chemical compound.

In the case of the coprecipitation of thallium with MoS_3, As_2S_3, SnS_2, Re_2S_7, PtS_2 and Ir_2S_3, and of In with CuS and Ag_2S, the ratio of Tl or In to Me is 1 : 1.

The coprecipitation of thallium with In_2S_3, PdS, Ru_2S_3 and Rh_2S_3 is characterised by curves with breaks at a Tl:Me ratio of 1 :2.

It is important to note that at a ratio in the solution of Tl to Re, Pt or Ir of 1 :1, the ratios in the solid phase are, respectively, 1 : 0·85, 1 : 0·95 and 1 : 0·87, and at ratios of Tl to Pd, Ru or Rh in the solutions of 1 : 2 these ratios are 1 : 0·42, 1 : 0·48 and 1 : 0·39, respectively.

We obtained an analogous picture for the coprecipitation of Tl with As_2S_3, SnS_2 and MoS_3, and also for In with CuS and Ag_2S.

Thus, the coprecipitation reaction, for example for the Tl^+ ion with Re_2S_7, takes place to the extent of only 85·4% by the equation

$$2Tl^+ + Re_2S_7{\cdot}nH_2S \rightleftharpoons 2TlReS_4{\cdot}(n - 1)H_2S + 2H^+.$$

In order that the coprecipitation reactions mentioned should take place quantitatively, a two-fold excess of Tl^+ ion in the solution is necessary. The investigation of coprecipitation in the systems mentioned which has been carried out permits the theoretical coprecipitation diagram characteristic for the formation of chemical compounds to be given (Fig. 12). All of the systems that we have studied correspond to this type of diagram, in which coprecipitation is connected with the formation of chemical compounds.

In the case of the coprecipitation of Tl with As_2S_3, SnS_2 and MoS_3, and of In with CuS and Ag_2S, the coprecipitation diagrams should have a similar form. The displacement of part of the curve with respect to the abscissae apparently resulted from the fact that for low concentrations of Tl^+ and In^{3+} the equilibrium state was not attained (Fig. 10.).

In the diagrams of this type, field A (Fig. 12) is characterised by parallel coprecipitation curves indicating proportionality between the amount of coprecipitated cation and its concentration in the solution. As is well known, such a situation is characteristic for solid solutions.

As the results of X-ray analysis have shown, in the range of concentrations of the second component corresponding to field A, the formation of a microdisperse system—a "colloidal" solid solution—takes place.

When the concentration of the cation in the solution is increased, a new field B appears on the diagram (Fig. 11). For the case of the formation of chemical compounds, the break in the curve is found at multiple ratios between their components. The formation of chemical compounds for the range of concentrations corresponding to field B was confirmed by analysis of the precipitates and by their X-ray diagrams. The composition of the solid phase as the concentration of the second component is increased within the range AB remains constant. Graphically, this is determined by the angle of inclination α of the coprecipitation curve.

As the experiments show, with an excess of thallium in the solution (Me:Tl = 1 : 4 — 1 : 16) its content in the solid phase exceeds the stoichiometric amount. This is particularly clearly expressed in the case of the coprecipitation of thallium with In_2S_3 and Ir_2S_3.

The phenomenon observed is obviously connected with the general property of chemical compounds of giving solid solutions with an excess of their components. A confirmation of the hypothesis expressed is the invariability of the distribution constant of the second component between the solution and the solid phase formed under these conditions. The capacity of chemical compounds for giving solid solutions with an excess of the second component explains the appearance on the diagram for the coprecipitation of thallium with Ir_2S_3 (Fig. 6) of a new field C, and with In_2S_3 of field D (Fig. 8).

It follows from the results given that the coprecipitation diagram in association with X-ray analysis of the solid phases obtained permits a fairly complete picture of the phenomenon to be obtained.

In conclusion, we should like to mention that the experimental material presented shows the importance of chemical compounds in the coprecipitation of cations with sulphides. Construction of the coprecipitation diagram makes it possible to obtain a complete picture of this process.

Acknowledgment—The authors express their thanks to Corresponding Member of the U.S.S.R. Academy of Sciences, I. P. Alimarin, for valuable advice on the investigation.

Zusammenfassung—Eine Untersuchung der Mitfällung von Thallium mit As_2S_3, SnS_2, MoS_3, Re_2S_7, PtS_2, PdS, Ru_2S_3, Rh_2S_3, Ir_2S_3 und In_2S_3 und von Indium mit CuS und Ag_2S mit physikochemischen Methoden zeigte, daß die Mitfällung auf der Bildung folgender

Verbindungen beruht: $TlAsS_2$, $TlSnS_2$, $TlMoS_2$, $TlReS_4$, $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$, $TlRh_2S_4$, Tl_3Ir_3S, $TlIn_2S_3$, $CuInS_2$ und $AgInS_2$. Eine für die Bildung von Verbindungen charakteristische Art von Mitfällungsdiagramm wurde aufgestellt und darauf die Phasen bestimmter Zusammensetzung entsprechenden Bereiche abgegrenzt. Es wurde gezeigt, daß sich bei der Mitfällung mikrodisperser Systeme "kolloide" feste Lösungen eines Sulfids im andern bilden.

Résumé—Une étude de la coprécipitation du thallium avec As_2S_3, SnS_2, MoS_3, Re_2S_7, PtS_2, PdS, Ru_2S_3, Rh_2S_3, Ir_2S_3 et In_2S_3, et de l'indium avec CuS et Ag_2S au moyen de l'analyse physico-chimique a montré que le phénomène est dû à la formation des composés suivants: $TlAsS_2$, $TlSnS_2$, $TlMoS_2$, $TlReS_4$, $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$, $TlRh_2S_4$, Tl_3Ir_3S, $TlIn_2S_3$, $CuInS_2$ et $AgInS_2$. On a établi un type de diagramme de coprécipitation caractéristique, pour le cas où il y a formation de composés chimiques, et on y a délimité les domaines correspondant aux phases de composition définie. On a montré qu'il se forme, lors de la coprécipitation, des systèmes microdispersés de solutions solides "colloïdales" d'un sulfure dans l'autre.

REFERENCES

[1] N. A. Rudnev, *Zhur. analit. Khim.*, 1953, **8**, 3.

[2] N. A. Rudnev and G. I. Malofeyeva, Mitteilungsblatt der Chemischen Gesellschaft in der DDR, Sonderheft, 1960, Analytische Chemie, p. 437.

[3] F. Feigl, *Z. analyt. Chem.*, 1924/1925, **65**, 25.

[4] *Idem, Z. anorg. Chem.*, 1926, **157**, 251.

[5] *Idem, ibid.*, 1926, **157**, 269.

[6] A. Okač, *Qualitative analytische Chemie.* Akademische Verlagsgesellschaft, Leipzig. 1960, i45, i47, i48.

[7] L. F. Hawley, *J. Phys. Chem.*, 1906, **10**, 654.

[8] *Idem, J. Amer. Chem. Soc.*, 1907, **29**, 1011.

[9] L. Bruner and J. Zawadzki, *Z. anorg. Chem.*, 1910, **65**, 139.

[10] H. Malfatti, *Z. analyt. Chem.*, 1909, **48**, 352.

[11] Ye. M. Nanobashvili, N. G. Shella and L. V. Ivanitskaya, *Soobshch. AN Gruz. SSR*, 1957, **19**, 557.

[12] Ye. M. Nanobashvili, Ye. G. Davitashvili and N. Ya. Shorgobiani, *Trudy Inst. Khim. AN Azerb. SSR*, 1959, **17**, 38.

[13] V. I. Davydov and N. P. Diyev, *Zhur. priklad. Khim.*, 1959, **32**, 441.

[14] N. A. Rudnev and L. I. Guseva, *Zhur. analit. Khim.*, 1956, **11**, 44.

[15] N. A. Rudnev and G. I. Malofeyeva, *Zhur. neorg. Khim.*, 1961, **6**, 453.

[16] N. A. Rudnev and A. A. Mazur, *Zhur. analit. Khim.*, 1957, **12**, 433.

[17] A. I. Kitaigorodskii, *X-ray Analysis of Microcrystalline and Amorphous Materials.* State Publishing House for Technical and Theoretical Literature, Moscow and Leningrad, 1952 (In Russian).

Talanta, 1964, Vol. 11, pp. 543 to 547. Pergamon Press Ltd. Printed in Northern Ireland

A THERMOGRAVIMETRIC STUDY OF ALUMINIUM OXINATE

C. J. KEATTCH
John Laing Research and Development Ltd., Manor Way, Boreham Wood
Hertfordshire, England

(*Received* 8 *August* 1963. *Accepted* 27 *September* 1963)

Summary—A thermogravimetric study of aluminium oxinate obtained by three different procedures has confirmed the view generally held that 150° is a suitable drying temperature. It has also been shown that this temperature is satisfactory, irrespective of the original moisture content of the precipitate. That a temperature of 700° is sufficient to obtain aluminium oxide is also confirmed. On the other hand, the statement by some workers that aluminium oxinate can be dried at 375° has not been substantiated.

INTRODUCTION

THERE is some confusion in the literature regarding the drying and decomposition temperatures of aluminium oxinate. Dupuis and Duval[1] studied this complex thermogravimetrically and found that it achieved constant weight between 102 and 220°, thus concluding that the drying temperature of 110° recommended by many workers is correct but too restrictive. In addition, they found that total destruction of organic matter and conversion to the oxide was only complete above 1000°.

However, Borrel and Paris,[2] also from thermogravimetric data, found that anhydrous aluminium oxinate is not obtained until 135° and that 110° is too low a drying temperature to obtain the anhydrous material. They further claimed that the complex is stable up to 375°, but beyond this temperature there is gradual decomposition until 700° when the oxide is formed, with an unexplained and anomalous weight change at 520°. Unlike Dupuis and Duval, they consider it unnecessary to raise the temperature to 1000° in order to destroy organic matter and suggest that Dupuis and Duval used too rapid a heating rate to obtain complete decomposition at 700°.

In his authoritative text-book on oxine and its derivatives, Hollingshead[3] comments on the above divergence of opinion as to the drying temperature of aluminium oxinate that "in view of the fact that many other workers have obtained satisfactory gravimetric determinations by drying in this range (100–135°) it would appear that further substantive evidence is necessary before the lower drying temperatures are discarded".

It was in an attempt to clarify the situation that this present work was initiated.

EXPERIMENTAL

In thermogravimetric measurements, many parameters can influence the final shape of the thermogram[4] and in the present context, it was considered that the following factors merited investigation:

(1) *Heating Rate*

It is reasonable to assume that the heating rate employed by Dupuis and Duval of approximately 6°/min was too fast to obtain good resolution of a thermogram. Borrel and Paris used a heating rate of 3°/min, which is considered to be a reasonable increment in order to achieve good resolution of a thermolysis curve. In the present work a heating rate of 3°/min was employed.

(2) *Moisture Content of Precipitate*

It has been demonstrated[5] that the moisture content of a precipitate can considerably alter the position of the thermogram plateau. Dupuis and Duval give no details as to the moisture content of their samples, although the published thermogram indicates that it is considerable. On the other hand, Borrel and Paris dried their precipitates on the filter crucible by drawing air at room temperature through the precipitate for 24–48 hr. In view of these two widely differing procedures and their possible influence on the shape of the thermolysis curve, undried and air-dried precipitates were studied in the current investigation.

(3) *Mode of Precipitation*

It is well known that different methods of forming precipitates influence the shape of the thermogram[6] and it appears feasible that this observation could apply in the present context. Dupuis and Duval precipitated aluminium oxinate by Berg's method[7] whereas Borrel and Paris, although saying that the oxinate was precipitated by the usual method, used a procedure which differed in detail from Berg's technique. It would not, of course, be practicable to study aluminium oxinate precipitated by all of the numerous published methods, but in addition to the two procedures mentioned above, it was considered worthwhile including the technique currently in use in the author's laboratory[8] because, again, this differs in detail.

In order that a comparison can be made, the essential details of the precipitation methods used in the current investigations are given below.

Method of Berg[7]

To an aluminium solution containing less than 100 mg of aluminium/ml were added 3–5 g of sodium acetate followed by a slight excess of oxine solution (3 g of oxine dissolved in 3 ml of glacial acetic acid, diluted to 100 ml with water and neutralised with aqueous ammonia). The mixture was stirred vigorously, warmed to 60–70° and the precipitated complex filtered, then washed with water until the washings were colourless.

Method of Borrel and Paris[2]

To 100 ml of $0{\cdot}0333M$ aluminium solution was added sufficient oxine solution ($0{\cdot}1M$ in $0{\cdot}2M$ hydrochloric acid) to give a 10% excess and the mixture warmed to 70–80°. The solution was neutralised with $0{\cdot}5M$ sodium carbonate, then buffered to about pH 7 with 15% w/v ammonium acetate solution. The mixture was boiled gently for 2–3 min, then maintained at 80° for 0·5 hr. The oxinate was filtered, washed twice by decantation with hot water, transferred to the filter crucible and washed further with hot water to remove the excess oxine.

Method of the British Ceramic Research Association[8]

To approximately 100 ml of neutralised aluminium solution, containing 15–35 mg of aluminium, were added 4 ml of 50% w/v hydroxylamine hydrochloride followed by 5 ml of freshly prepared 1% w/v *o*-phenanthroline [1g dissolved in 100 ml of acetic acid (1 + 1)]. The solution was heated to 40–50°, 20 ml of 5% w/v oxine solution added (5 g of oxine dissolved in 12 ml of glacial acetic acid and diluted to 100 ml with water) followed by 40 ml of 40% w/v ammonium acetate solution, added slowly and with stirring. The solution was heated to 70° with stirring and maintained at this temperature for 10 min, stirring periodically. After cooling for 30 min, the precipitate was filtered and washed thoroughly with warm water (40–50°).

Portions of the oxinate obtained by these three different procedures were removed from the filter crucible immediately after washing was complete and stored in well-stoppered containers. The remainder of the precipitate in each case was dried by drawing air through the filter crucible for 48 hr.

A sample of each preparation, weighing between 250 and 350 mg, was transferred to a prefired recrystallised alumina crucible and heated in air on a Stanton thermobalance, Model HT-SM, which was programmed for a linear temperature rise from room temperature to 1400° over 8 hr (3°/min nominal) and a chart speed of 6 in./hr. The thermograms obtained are given in Fig. 1.

DISCUSSION

From the thermograms, it is apparent that all of the samples have achieved constant weight at 160°. Thus it can be concluded that the drying temperature of 150° recommended by many workers is satisfactory, irrespective of the original

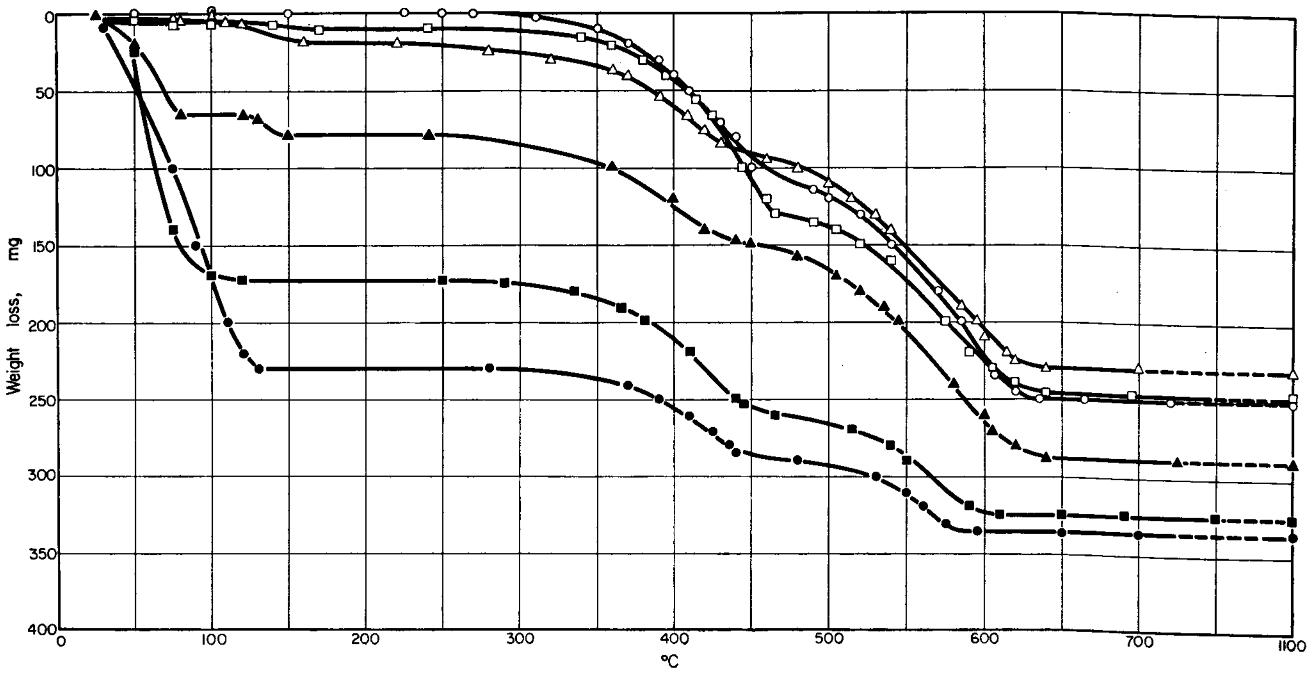


FIG. 1.—Thermograms of aluminium oxinate obtained by different precipitation procedures:

△—Brit. Ceram. Res. Assoc., air dried;
▲—Brit. Ceram. Res. Assoc., undried;
○—Borrel and Paris, air dried;
●—Borrel and Paris, undried;
□—Berg, air dried;
■—Berg, undried.

moisture content of the precipitate. Although only three different methods of precipitation have been investigated, it is reasonable to assume that 150° is a suitable drying temperature for aluminium oxinate precipitated by any published method.

The results also confirm the conclusion of Dupuis and Duval that a drying temperature of 110° is satisfactory, but too restrictive. However, contrary to the findings of Borrel and Paris, the thermograms of all of the samples demonstrate, quite conclusively, that the precipitate is not stable at 375° and independent attempts to dry aluminium oxinate at this temperature resulted in complete failure. On another point, the thermograms indicate that aluminium oxide is formed at approximately 600°. There is little doubt that, as Borrel and Paris remark, 700° is a sufficiently high temperature to obtain the oxide and that Dupuis and Duval used too high a heating rate to obtain complete decomposition at this temperature.

The anomalous weight change at 520° described by Borrel and Paris is manifest in the present work by a change in slope occurring at about 460°, which suggests the formation of an intermediate compound. It is doubtful whether it would be possible to isolate this intermediate, because it has been shown[9] that the decomposition of metal oxinates is a complicated process and the exact mechanism of decomposition is not known.

CONCLUSIONS

Using three different procedures for precipitating aluminium oxinate, it has been confirmed that a satisfactory drying temperature for the complex is 150°. It has been shown that this temperature can be used irrespective of the original moisture content. Contrary to the findings of Borrel and Paris, spurious results were obtained on drying the complex at 375°. Aluminium oxide is formed at temperatures above 600° and failure to obtain complete decomposition at temperatures much in excess of this value strongly indicates too high a heating rate.

Aluminium oxinate, prepared by precipitation from homogeneous solution (PFHS), has also been studied. The procedure used was according to Marec, Salesin and Gordon[10] except that the 8-acetoxyquinoline was purchased. (B. Newton Maine Ltd., Silsoe, Bedfordshire, England.)

As was to be expected, the thermolysis curves of both undried and air-dried samples were very similar to those depicted in Fig. 1. They confirm that 150° is a suitable drying temperature for aluminium oxinate precipitated by this technique but that drying at 375° results in decomposition.

The major difference in the thermolysis curves of aluminum oxinate prepared by PFHS is that aluminium oxide is not formed until a little over 700°. This is to be expected as PFHS results in denser crystals.

Acknowledgment—The author thanks the Directors of John Laing Research and Development Ltd., for permission to publish this paper.

Zusammenfassung—Eine thermogravimetrische Untersuchung an auf drei verschiedene Arten erhaltenem Aluminiumoxinat bestätigte die allgemeine Ansicht, daß 150° eine geeingete Trocknungstemperatur ist. Es wurde auch gezeigt, daß diese Temperatur unabhängig vom ursprünglichen Feuchtigkeitsgehalt des Niederschlags ausreicht. Es wurde auch bestätigt, daß 700° zur Bildung von Aluminiumoxyd ausreichen. Andererseits ließ sich nicht bestätigen, daß Aluminiumoxinat bei 375° getrocknet werden kann.

Résumé—Une étude thermogravimétrique de l'oxinate d'aluminium obtenu par trois procédés différents a confirmé l'opinion généralement admise que 150°C constitue une bonne température désséchante. Il a pu être montré que cette température est satisfaisante pour l'humidité du précipité. Le fait que 700°C soient suffisants pour obtenir l'oxyde d'aluminium a été également confirmé. D'autre part, les conclusions de certains chercheurs qui indiquent 375° comme température de dissociation de l'oxinate d'aluminium n'ont pu être confirmés.

REFERENCES

[1] T. Dupuis and C. Duval, *Analyt. Chim. Acta*, 1949, **3**, 191.
[2] M. Borrel and R. Paris, *ibid.*, 1950, **4**, 267.
[3] R. G. W. Hollingshead, *Oxine and its Derivatives.* Butterworths, London, 1954, Vol. 1, p. 88.
[4] A. E. Newkirk, *Analyt. Chem.*, 1960, **32**, 1558.
[5] J. Rynasiewicz and J. F. Flagg, *ibid.*, 1954, **26**, 1506.
[6] C. Duval, *Inorganic Thermogravimetric Analysis.* Elsevier, London, 2nd Ed., 1963, pp. 226, 528.
[7] R. Berg, *Z. analyt. Chem.*, 1927, **71**, 369; *Das Oxin.* F. Enke, Stuttgart, 2nd Ed., 1938.
[8] British Ceramic Research Association, Chemical Analysis Sub-Committee, *Trans. Brit. Ceram. Soc.*, 1952, **51**, 438.
[9] W. W. Wendlandt and G. R. Horton, *Analyt. Chem.*, 1962, **34**, 1098.
[10] D. J. MAREC, E. D. SALESIN and L. GORDON, *Talanta*, 1961, **8**, 293.

Talanta, 1964, Vol. 11, pp. 549 to 571. Pergamon Press Ltd. Printed in Northern Ireland

NEW STUDIES ON CALCIUM OXALATE MONOHYDRATE

A GUIDE TO THE INTERPRETATION OF THERMOGRAVIMETRIC MEASUREMENTS

E. L. SIMONS and A. E. NEWKIRK
Research Laboratory, General Electric Company, Schenectady, New York, U.S.A.

(*Received* 21 *August* 1963. *Accepted* 20 *October* 1963)

Summary—The pyrolysis of calcium oxalate monohydrate in air occupies a unique place in the literature of thermogravimetry. Not only was a thermogram for this reaction the first pyrolysis curve published by Duval and his collaborators, but Duval and others have suggested that it can be used as a reference substance for judging the performance of a thermobalance. However, the pyrolysis of calcium oxalate monohydrate under a variety of conditions gives rise to considerable differences in its thermograms. The effects of sample size, heating rate, atmosphere and container geometry are presented in a series of paired thermograms, and the differences are accounted for with the aid of additional evidence from differential thermal analysis and from combustion train experiments. Variations in atmosphere are particularly important, and the atmospheres studied are dry nitrogen, humidified nitrogen, dry air, humidified air, dry oxygen, dry carbon dioxide and dry carbon monoxide. Even subtle variations in the shape of a thermogram obtained on a reliable balance may reflect the complexity of the reactions that produce the more noticeable over-all weight changes. Results presented in this report thus delineate conditions for the use of calcium oxalate monohydrate as a thermogravimetric reference substance, and show that its behaviour under controlled conditions in a thermobalance can provide an unusually versatile guide to the interpretation of thermogravimetric measurements.

INTRODUCTION

THE pyrolysis of calcium oxalate monohydrate in air occupies a unique place in the literature of dynamic thermogravimetry. A thermogram for this reaction (Fig. 1) was the first pyrolysis curve published by Duval and his collaborators[42] in their comprehensive study of the thermogravimetric behaviour of analytical precipitates, and was

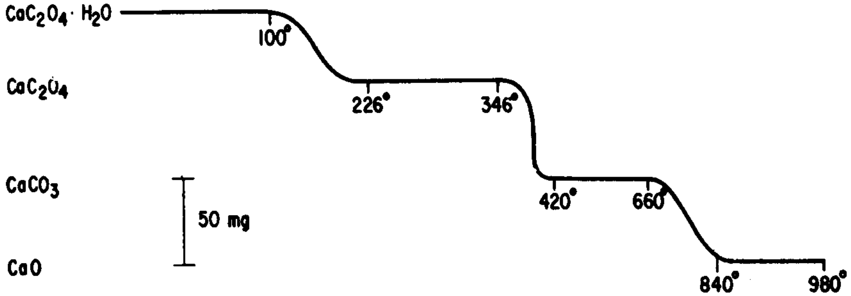


FIG. 1.—Pyrolysis curve of calcium oxalate monohydrate as published by Peltier and Duval.[42]

singled out by Duval for special mention in his book.[13] Because the thermogram's unusual sequence of consecutive reactions was characterised by four parallel, horizontal plateaux, corresponding successively to calcium oxalate monohydrate, calcium oxalate, calcium carbonate and calcium oxide, the material was used by Duval[12] "to adjust the thermobalances after they have been set up, cleaned, or repaired." He further claimed that the thermogravimetric measurements on this material with a photographic recording Chevenard thermobalance were accurate and reproducible enough to permit students to obtain reliable values for the atomic weight of carbon from the dimensions of thermograms obtained as an instructional exercise.[13] Subsequently, Barcia Goyanes[2] and Wilson[57] suggested that the extremities of the plateaux in this thermogram be used as temperature calibration points for a thermobalance, as if they were characteristic transition temperatures.

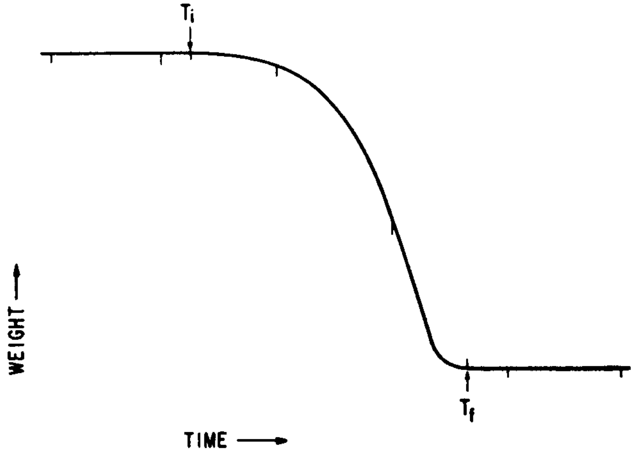


FIG. 2.—Schematic thermogram for general single-stage reaction: $A_{(solid)} = B_{(solid)} + C_{(gas)}$.

Previous work in this Laboratory has demonstrated that the accuracy and precision of measurements with a Chevenard pen-recording thermobalance (which has the same suspension and sensitivity as the photographic recording balance) are below the level required for atomic weight work[48] and that the temperature limits of a plateau are not a property of the sample alone.[36] This report presents thermograms for calcium oxalate monohydrate pyrolysed under a variety of conditions and attempts to provide a consistent explanation for all of the observed differences, using additional data from differential thermal analysis measurements and from combustion train experiments. The results of these studies show that if calcium oxalate monohydrate is pyrolysed under carefully controlled conditions in a thermobalance, it can serve as a yardstick for judging the performance of the instrument and can provide an unusually versatile guide to the interpretation of thermogravimetric measurements.

CHARACTERISTICS OF SINGLE-STAGE REACTIONS

The thermogram of Fig. 2 has been drawn to represent the general reaction

$$A_{(solid)} = B_{(solid)} + C_{(gas)}.$$

Two temperatures may be selected as characteristic of any single-stage non-isothermal reaction: T_i (initial temperature) is the temperature at which the cumulative weight-change reaches a magnitude that the thermobalance can detect, and T_f (final temperature) is the temperature at which the cumulative weight-change first reaches its maximum value, corresponding to complete reaction. Although T_i may be the lowest temperature at which the onset of a weight-change can be observed in a given experiment, it is neither a transition temperature in the phase rule sense,[35] nor is it a true decomposition temperature below which the reaction rate suddenly becomes zero.[20,21,24,25] Because the value of T_i depends upon the interaction of many variables, it shall be called the *procedural decomposition temperature*,[36] a term introduced by Doyle[10] in reporting his thermogravimetric studies of the pyrolysis of polymers. At a linear heating rate, T_f must be greater than T_i, and the difference ($T_f - T_i$) will be called the *reaction interval.* For an endothermic decomposition, T_i and T_f both increase with increasing heating rate, the effect being greater for T_f than for T_i, as has been clearly shown by Richer[45] and others.[8,34,36]

SIGNIFICANCE OF TEMPERATURE IN DYNAMIC THERMOGRAVIMETRY

At this point it is advisible to comment upon the significance of temperature as a variable in dynamic thermogravimetry. The fundamental datum produced by a recording thermobalance is a record that shows the variation with time of some quantity whose changes may be related in magnitude to changes in the weight of the sample. The foundations of modern dynamic thermogravimetry were laid in the early 1920's by Guichard,[22,23] who proposed that the method of continuous weighing be applied to "the study of all reactions that cause the weight of any solid to vary in one way or another . . . in a selected atmosphere, while the temperature is raised at a rate nearly proportional to the time, and slowly enough." Although Guichard did not explicitly specify the temperature to be measured, it is apparent from his work and that of his students that he referred to the temperature of the furnace atmosphere and not to that of the sample.[11,53,54]

Guichard had insisted, since the beginning of his studies, "on the necessity of realising a very regular rise of temperature." He pointed out that "there is a risk that every irregularity in this increase may appear on the curve of weight *vs.* time and complicate its interpretation." Such regularity in heating rate can be achieved in the furnace atmosphere but not in the sample, whose rate of temperature rise changes with the onset of each exothermic or endothermic phase transition or chemical change. These internally generated changes in the rate of sample temperature rise, of course, provide the basis for the widely used method of differential thermal analysis. Both differential thermal analysis and dynamic thermogravimetric analysis require a linear furnace heating rate. In differential thermal analysis one detects the onset of reactions or transitions in a sample by observing the perturbations in what would otherwise be a regular rate of increase in sample temperature. In thermogravimetry one detects and measures those transformations that produce a change in the weight of a sample. The only independent temperature variable in either technique is the heating rate of the furnace. The changes in sample weight and temperature are both consequences of the chemical and physical changes produced in a sample when it is brought into contact with a given atmosphere whose temperature is changing at a predetermined rate.

In this investigation an independent record was kept of the furnace temperature as a function of time, which record also served to verify the linear heating rate that had been set on the furnace controller. The temperature markings on the thermograms were established by coupling the temperature and weight recorders so that a pip was automatically introduced into the pyrolysis curve at each integral 100-degree reading of the furnace temperature. The pips could also have been introduced after the run by juxtaposition of the weight-time curve with the separate record of furnace temperature as a function of time. Values of T_i and T_f were interpolated between 100-degree markings.

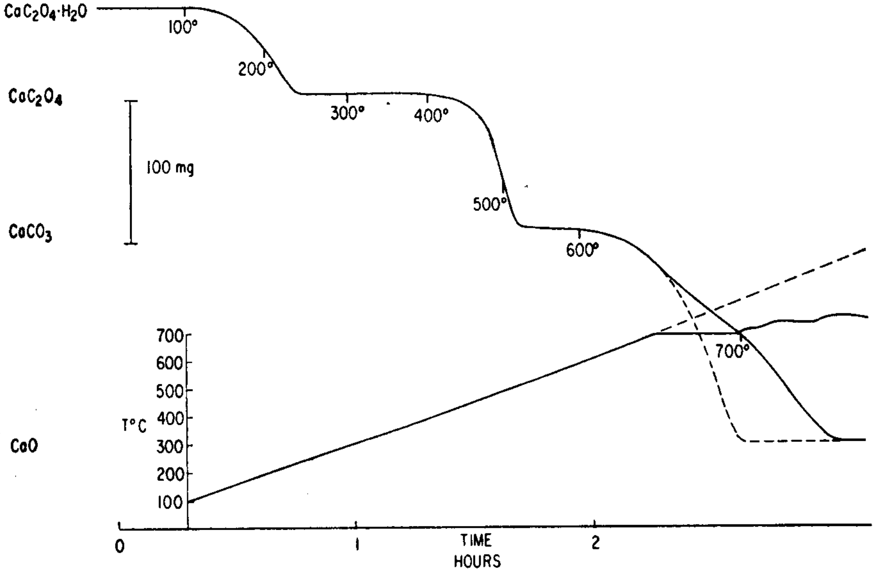


FIG. 3.—Effect of perturbation in rate of heating upon thermogram for calcium oxalate monohydrate (500 mg, platinum dish, flowing dry nitrogen):
– – – unperturbed rate of heating.

It is particularly risky to try to record a thermogram directly by feeding the weight and temperature signals to the two inputs of an X-Y recorder. Unexpected disturbances that sometimes occur in the heating rate or thermocouple response can produce artificial perturbations in the weight-temperature record. Only a separate temperature-time record can disclose these adventitious effects and permit effects caused solely by changes in sample weight to be distinguished from them.[27] Fig. 3 shows the thermobalance record of a pyrolysis of calcium oxalate monohydrate during which the temperature controller became stuck at 695°, for a period of time, after which it produced an irregular temperature rise up to about 750°. The dashed curve shows the course that the thermogram would have taken had the linear heating rate of 300 degree/hr been maintained above 695°. The perturbation in the recorded curve can be properly understood only in the light of the independent record of temperature as a function of time. Had an X-Y recorder been used for this run, the period of constant temperature would have been represented by a vertical line at 695°. Although such an abrupt change in the slope of the curve would probably have been suspect, more subtle, but nonetheless significant changes in heating rate could pass completely unnoticed in a direct recording of weight *vs.* temperature.

CHARACTERISTICS OF MULTI-STAGE REACTIONS

Successive, non-overlapping reactions

Under certain conditions, the thermogram for a sequence of successive decompositions, such as occurs during the pyrolysis of calcium oxalate monohydrate

$$CaC_2O_4{\cdot}H_2O = CaC_2O_4 + H_2O$$

$$A_{(s)} = B_{(s)} + \text{gas} \qquad (1)$$

$$CaC_2O_4 = CaCO_3 + CO$$

$$B_{(s)} = C_{(s)} + \text{gas} \qquad (2)$$

$$CaCO_3 = CaO + CO_2$$

$$C_{(s)} = D_{(s)} + \text{gas} \qquad (3)$$

can be considered as the composite of the thermograms for the individual stages. This is shown in Fig. 4, in which are superimposed the thermograms that were obtained on separate days by heating in air, at 300 degree/hr, 500 mg of calcium oxalate monohydrate and equivalent quantities of the anhydrous oxalate and of calcium carbonate, each in a porcelain crucible. The initial stages of the latter two curves are indicated by broken lines. Thermograms 4(B) and 4(C) are identical with 4(A) at temperatures above their intersections.

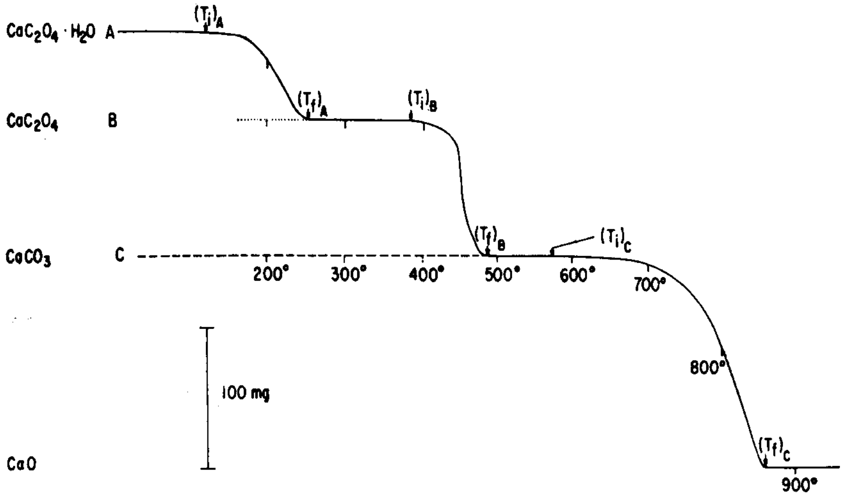


FIG. 4.—Thermograms for successive non-overlapping reactions (porcelain crucible, ambient air, 300 degree/hr):
——— 500 mg of calcium oxalate monohydrate,
...... 438 mg of calcium oxalate,
– – – – 343 mg of calcium carbonate.

It is not evident from this reproduction that the true value of $(T_i)_B$ is about 390°. The position of $(T_i)_B$ shown in this figure was chosen for illustrative purposes only.

Although temperature $(T_f)_A$ marks the beginning of the plateau for calcium oxalate, its value is determined by the interaction between the heating rate, the sample size and the rate of dehydration of calcium oxalate monohydrate; it cannot be interpreted as setting a lower limit to the thermal stability of the anhydrous salt. Temperature $(T_f)_A$ lies on the calcium oxalate plateau only because, under the conditions of the experiment, the dehydration reaction was complete before the temperature reached the value of $(T_i)_B$, the procedural decomposition temperature of the anhydrous salt. When calcium oxalate, previously dehydrated at 175°, was the starting material, the thermogram, beginning at level B, showed no perturbation as it passed through $(T_f)_A$. The calcium carbonate plateau, of course, bears the same relationship to its precursor as the calcium oxalate plateau bears to the monohydrate.

The exact superposition of the independently determined thermograms of Fig. 4 could have been achieved only if the reactions being studied were indeed successive and non-overlapping, and only if the characteristics of the thermobalance remained constant over the period of days covered by the experiments.

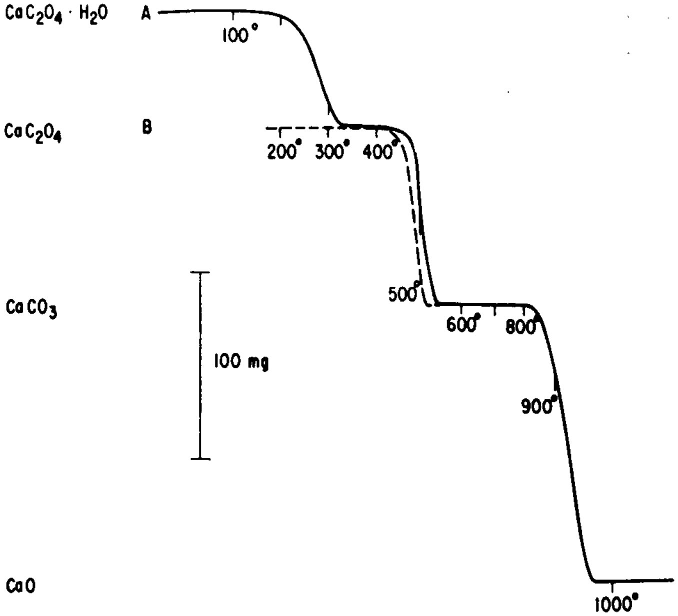


FIG. 5.—Thermograms for successive, partially overlapping reactions (porcelain crucible, ambient air, 600 degree/hr):
——— 500 mg of calcium oxalate monohydrate,
- - - - 438 mg of calcium oxalate.

Successive, partially overlapping reactions

The exact superposition of Fig. 4 is not characteristic of the pyrolysis of calcium oxalate monohydrate under all conditions. As noted earlier, both T_i and T_f for a given reaction rise as the heating rate is increased, the effect being more pronounced for T_f. The consequences of this are shown in Fig. 5, in which are superimposed the thermograms that were obtained by repeating two of the pyrolyses of Fig. 4, but at a heating rate of 600 degree/hr. The intermediate plateau for calcium carbonate is still clearly defined, but it begins at a higher temperature.[36] On the other hand, the formation of anhydrous calcium oxalate as an intermediate in the pyrolysis of the monohydrate is no longer marked by a true plateau, but simply by a change in the slope of the thermogram. At the higher heating rate the dehydration reaction on curve 5(A) was not complete by the time the furnace temperature had reached about 350°, which is the procedural decomposition temperature indicated for the anhydrous salt on curve 5(B). During the latter part of pyrolysis 5(A), therefore, water and carbon monoxide were being evolved simultaneously,[43] and at the point where the cumulative weight loss reached level B the sample crucible contained anhydrous calcium oxalate and a small amount of both the monohydrate and calcium carbonate.

A careful examination of the original thermograms discloses that curve 5(A) lies above curve 5(B) even in the region between 300° and 400°, and does not become coincident with it until the calcium carbonate plateau is reached. By increasing the heating rate from 300 to 600 degree/hr the initial sequence of two successive decompositions has been transformed to a sequence of two partially overlapping or simultaneous decompositions, the thermogram for which is not an exact composite of the individual stages.

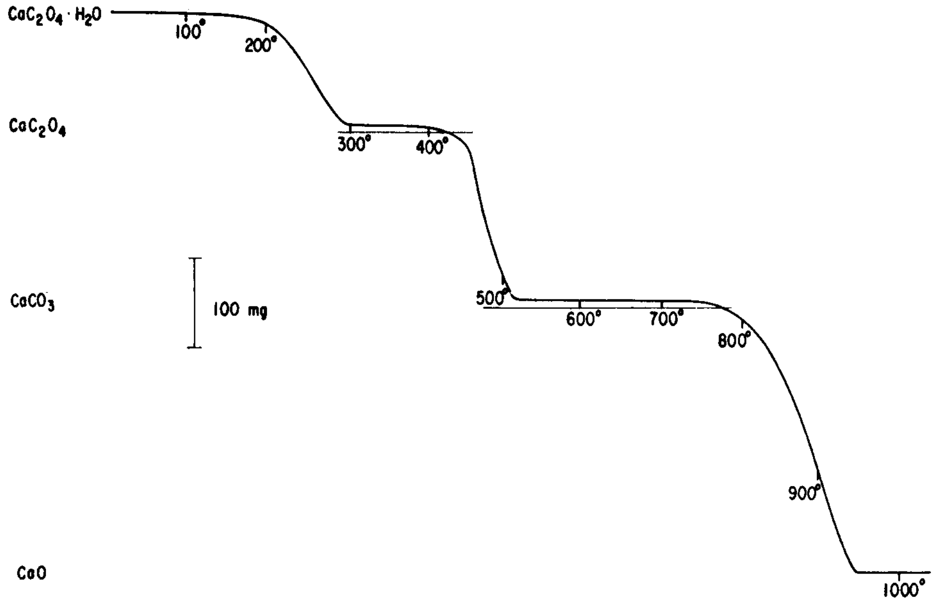


FIG. 6.—Thermogram for calcium oxalate monohydrate (1·019 g, porcelain crucible, ambient air, 300 degree/hr).

The transformation of a true plateau for anhydrous calcium oxalate into a curve like that of Fig. 5(A) was also produced by keeping the heating rate at 300 degree/hr, but increasing the sample weight from 0·5 g to approximately 1 g (Fig. 6). With more water in the initial sample, complete dehydration was not achieved before the procedural decomposition temperature for the anhydrous salt was reached, even at 300 degree/hr. This parallelism between the effects of heating rate and sample weight will be examined more closely in a subsequent section of this report.

At this point the following general conclusions may be drawn from the foregoing experiments on the multi-stage pyrolysis of calcium oxalate monohydrate:

1. *The appearance of a plateau for a compound on a dynamic thermogram does not necessarily imply that the compound is isothermally stable, either in a thermodynamic or practical sense, at all or any temperatures that lie on that plateau.* The temperature limits between which it extends apply only to the particular conditions of that pyrolysis.[5,20,44]

Certainly, none of the curves in Figs. 4, 5 or 6 can be used to set an upper limit to the isothermal stability of calcium carbonate in air. Similarly, anhydrous calcium oxalate undergoes slow isothermal decomposition in air at 300°, even though this temperature lies on the true plateau observed for that compound in Fig. 4.[43]

2. *If the thermogram obtained for a multi-stage reaction has no intermediate portion in which the sample weight remains constant with time over a range of temperature, one can make the reasonable inference that the reactions leading to the formation and to the subsequent decomposition of the intermediate are not independently sequential, but at least partly overlap.* The weight level at which a bend or change of slope occurs in the thermogram for such a pair of successive but overlapping reactions depends upon the relative amount of product B that has been formed by the time its procedural decomposition temperature has been reached and upon the relative rates of decomposition of A and B.

3. *In the absence of a true plateau, which can appear only if* $(T_f)_A \leqslant (T_i)_B$, *one cannot determine from a thermogram for successive reactions exact values for either* $(T_f)_A$, $(T_i)_B$, *or the stoichiometric weight level of B,[4] although a reasonable inference as to the latter can often be made.* There is little doubt, for example, that the gently sloping portion of Fig. 5 indicates the formation of anhydrous calcium oxalate.

CHARACTERISTICS OF INDIVIDUAL REACTIONS OF $CaC_2O_4 \cdot H_2O$

Among the factors that affect the thermogravimetric behaviour of calcium oxalate monohydrate are the reversibility of each stage of the pyrolysis and the enthalpy change that accompanies each of the individual reactions. The pertinent data are summarised in Table I.

TABLE I

Reaction	Heat of reaction ($\Delta H^\circ_{298^\circ K}$ kcal/mole)[47]	Reversibility
(1) $CaC_2O_4 \cdot H_2O = CaC_2O_4 + H_2O$	13·3*	Reversible[43]
(2) $CaC_2O_4 = CaCO_3 + CO$	15·5*	Irreversible[43,58]
(3) $CaCO_3 = CaO + CO_2$	42·5	Reversible

* Heat of formation of CaC_2O_4 estimated from tabulated values for the di- and monohydrates.

Reactions (1) *and* (3)

Both of these reactions are endothermic and reversible. In their thermogravimetric work, Peters and Wiedemann[43] showed that calcium oxalate monohydrate, after dehydration at about 280°, could be regenerated by allowing the anhydrous salt to cool to room temperature in humidified air. The effect of carbon dioxide in markedly raising the procedural decomposition temperature and decreasing the reaction interval for calcium carbonate has been clearly demonstrated by these workers and by Richer and Vallet.[44,45] For any given atmosphere containing carbon dioxide, the procedural decomposition temperature must be equal to or greater than the temperature at which the dissociation pressure of calcium carbonate reaches the partial pressure of carbon dioxide in that atmosphere.[28]

Reaction (2)

Thermal measurements by several investigators[14,41,49,56] have shown that the decomposition of anhydrous calcium oxalate is endothermic in an inert atmosphere, but becomes strongly exothermic in an oxidising atmosphere. These results have been confirmed in a Chevenard thermobalance. With the balance mechanism locked and a Pt-Pt, 10% Rh thermocouple inserted into the powdered sample, the difference between the sample temperature and the furnace temperature was recorded as a function of the furnace temperature, and the tracings shown in Fig. 7 were obtained from experiments made in flowing dry nitrogen and oxygen.

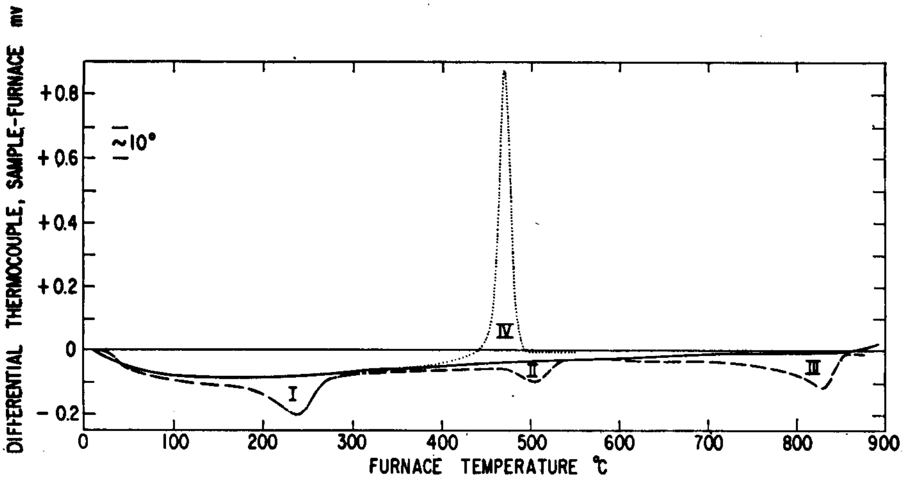


FIG. 7.—Differential thermal measurements on calcium oxalate monohydrate (500 mg):
——— inert sample (ignited calcium oxide),
– – – – calcium oxalate monohydrate in dry nitrogen,
...... calcium oxalate monohydrate in dry oxygen.

The exothermic peak observed in oxygen (and, with a more complex shape, in air) has been attributed by the investigators previously cited to the formation of carbon dioxide by oxidation of the carbon monoxide produced in the decomposition of the oxalate. The heat evolved/mole of carbon monoxide oxidised in the reaction

$$CO + 0{\cdot}5O_2 = CO_2 \qquad (4)$$

is 67·7 kcal at 700°K,[7] which is about four times larger than the heat absorbed by reaction (2). Reaction (4) has also been postulated to explain the exothermic effects noted when thorium oxalate was decomposed under oxidising conditions.[6,38]

The evidence to support the hypothesis that reaction (4) can also occur during the pyrolysis of calcium oxalate is presented in the following section.

DECOMPOSITION OF ANHYDROUS CALCIUM OXALATE

A weighed sample of calcium oxalate monohydrate in a platinum boat was loaded into a combustion tube and heated overnight at 125° in a stream of dry nitrogen to effect complete dehydration. Then, as in the method used by D'Eye and Sellman[9] for studying the thermal decomposition of thorium oxalate, the modified combustion train shown in Fig. 8 was assembled, and isothermal decompositions of the anhydrous salt were carried out for 3 hr at 420° with a stream of suitable carrier gas passing over the sample at a rate of 20 ml/min.

The gas, after leaving the pyrolysis chamber, passed through a series of tubes filled, successively, with Ascarite, hot copper oxide at 700° and Ascarite. Any carbon dioxide in the exit gas stream was trapped in the first Ascarite tube; any carbon monoxide in the exit gas stream was oxidised by the hot copper oxide and subsequently absorbed as carbon dioxide in the last absorption tube.

The results obtained with dry air and dry nitrogen as the carrier gases are given in Table II, to which the following comments are pertinent:

1. The dehydration of the samples was complete at 125°.

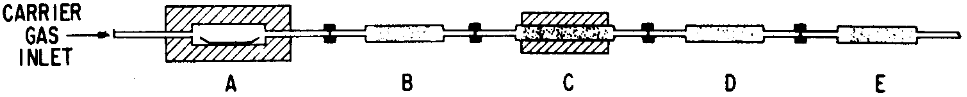


FIG. 8.—Schematic illustration of modified combustion train for experiments with dry nitrogen and dry oxygen:

A—furnace with combustion tube and platinum boat,
B—Ascarite absorption tube,
C—furnace with tube of copper oxide,
D—Ascarite absorption tube,
E—Ascarite tare tube.

2. The amount of calcium oxalate that decomposed in 3 hr at 420° was significantly greater in dry air than in dry nitrogen.

3. In dry air (run 1), the primary gaseous product of the decomposition of anhydrous calcium oxalate at 420° was carbon monoxide. Virtually all of this product had been oxidised to carbon dioxide by the time the gas stream reached the first Ascarite tube, and the total moles of carbon dioxide trapped by both Ascarite tubes is in excellent agreement with the weight loss of the sample, calculated as moles of carbon monoxide.

4. In dry nitrogen (run 2) most of the carbon monoxide produced during the decomposition of the anhydrous calcium oxalate left the reaction zone unchanged and appeared as carbon dioxide only after passing through the hot copper oxide tube. However, a significant amount of carbon dioxide was absorbed in the first Ascarite tube, between the pyrolysis furnace and the copper oxide furnace. In a nitrogen atmosphere, this carbon dioxide could not have been produced by oxidation of carbon monoxide, but must have arisen from the disproportionation reaction

$$CO = 0{\cdot}5CO_2 + 0{\cdot}5C \qquad \Delta H_{700^\circ K} = -20{\cdot}7\ \text{kcal}^7 \qquad (5)$$

On this basis, the following material balance can be made:

$$\begin{array}{lrl} \text{CO (mmole) undergoing disproportionation} & = 2(0{\cdot}36) & = 0{\cdot}72 \\ \text{CO (mmole) undergoing oxidation by CuO} & & = \underline{2{\cdot}30} \\ & \text{Total} & = 3{\cdot}02 \\ \text{CO (mmole) calculated from weight loss} & & = 2{\cdot}90 \end{array}$$

Thus, in dry nitrogen as in dry air, the primary gaseous product of the decomposition of anhydrous calcium oxalate at 420° was carbon monoxide.

The disproportionation reaction has been observed by Glasner and Steinberg[17–19] in their studies of the thermal decomposition of rare earth oxalates in vacuum. Qualitative evidence for its role in the vacuum decomposition of sodium oxalate and of alkaline earth oxalates has been reported by Günther and Rehaag[26] and by Wöhler and Schuff,[58] and it has been observed by D'Eye and Sellman[9] when thorium oxalate was decomposed in a stream of nitrogen.

Further evidence for disproportionation in these experiments was the grey discoloration observed in the sample that had been partially decomposed in a stream of nitrogen; the residue from the air run was pure white. The intensity of the discoloration could be reduced by passing air over the hot residue. A greyish-brown discoloration was also observed in the residues from thermogravimetric runs made in dry nitrogen.

To confirm the reported irreversibility of the decomposition of anhydrous calcium oxalate,[43,58] runs were made at 420° in a stream of dry carbon monoxide; this

TABLE II.—PYROLYSIS OF $CaC_2O_4{\cdot}H_2O$ IN MODIFIED COMBUSTION TRAIN

Run no.	1	2	3(a)	3(b)
Atmosphere	Dry air	Dry N_2	Humid N_2	Dry O_2
Wt. $CaC_2O_4{\cdot}H_2O$, *mg*	1331·5 (9·11 mmole)	1105·1 (7·56 mmole)	1109·0 (7·59 mmole)	Run 3(b) was made on residue remaining from 3(a)
Wt. loss in N_2 at 125° (stoich. = 12·33%), *mg*	165·2 (12·40%)	139·0 (12·58%)	140·0 (12·62%)	
Wt. loss in carrier gas at 420° for 3 hr, *mg*	93·2 (≡ 3·33 mmole CO)	81·2 (≡ 2·90 mmole CO)	99·6 (≡ 3·56 mmole CO)	48·6 (≡ 1·74 mmole CO)
Wt. CO_2 absorbed in 1st Ascarite tube, *mg*	140·0 (≡ 3·18 mmole CO_2)	15·7 (≡ 0·36 mmole CO_2)	89·9 (≡ 2·04 mmole CO_2)	77·8 (≡ 1·77 mmole CO_2)
Wt. CO_2 absorbed in 2nd Ascarite tube, *mg*	1·7 (≡ 0·04 mmole CO_2)	101·2 (≡ 2.30 mmole CO_2)	39·5 (≡ 0·90 mmole CO_2)	0·0
Total CO_2 absorbed, *mg*	141·7 (≡ 3·22 mmole CO_2)	116·9 (≡ 2·66 mmole CO_2)	129·4 (≡ 2·94 mmole CO_2)	77·8 (≡ 1·77 mmole CO_2)
Wt. H_2O absorbed in Anhydrone tube, *mg*			12·8 (≡ 0·71 mmole H_2O)	0·7 (≡ 0·04 mmole H_2O)

atmosphere neither prevented the decomposition of the pure salt nor reversed the decomposition of a partially decomposed sample. This observation means, of course, only that if the reaction is reversible, its equilibrium pressure of carbon monoxide at 420° is greater than 1 atmos.

The following conclusions may be drawn from the foregoing combustion train experiments and from the thermal measurements described in the preceding section:

1. In both oxidising and inert atmospheres the primary endothermic formation of carbon monoxide from anhydrous calcium oxalate is accompanied, to varying degrees, by one or more secondary exothermic reactions that produce carbon dioxide from carbon monoxide.
2. The direct oxidation of carbon monoxide by oxygen occurs more readily than the disproportionation reaction.
3. The heat evolved during direct oxidation of carbon monoxide by oxygen raises the temperature of the remaining sample and solid product at a rate greater than the heating rate of the furnace, and, as a result, the decomposition is more rapid in dry air than in dry nitrogen.

EFFECT OF VARIABLES UPON A DYNAMIC THERMOGRAM

The characteristics of the separate stages in a multi-stage pyrolysis have an important bearing on the interpretation of thermogravimetric data. In particular, the pyrolysis of calcium oxalate monohydrate, with its sequence of alternating reversible and irreversible reactions, coupled with secondary reactions between components of the atmosphere and a primary decomposition product, provides an ideal vehicle for demonstrating the effects of many variables upon the shape of a dynamic thermogram. In the remainder of this report, a series of comparison thermograms is presented to show these effects.

Geometry of sample container

Several investigators have recommended that for thermogravimetric measurements the sample should be loosely packed in a shallow dish in order to facilitate gaseous exchange between the sample and the atmosphere that surrounds it.[3,8,16,37,41] Indeed, Garn and Kessler[16] have declared, "That the traditional crucibles are useless in thermogravimetry is essentially true. In a few cases crucibles are acceptable . . . In controlled atmosphere work, where the atmosphere is solely the gas involved in the reaction, the geometry of the container is immaterial."

As can now be shown with calcium oxalate, the geometry of the container is also immaterial if no interaction is possible between the solid phase and the gaseous atmosphere or products. The pyrolysis of 500 mg of calcium oxalate monohydrate was conducted in flowing dry carbon dioxide using both a porcelain crucible and a quartz dish as sample holders. The thermograms in Fig. 9 are identical above about 275°, which marks the completion of the dehydration reaction in the crucible. As expected, the loss of water occurred more readily from the shallow dish than from the crucible. On the other hand, the shape of the container had no effect upon the decomposition of anhydrous calcium oxalate because this reaction is not reversible, and in a carbon dioxide atmosphere no important diffusion-controlled secondary reactions can occur. The shape of the container also had no effect upon the dissociation of calcium carbonate because this reaction is reversible, and the atmosphere used was

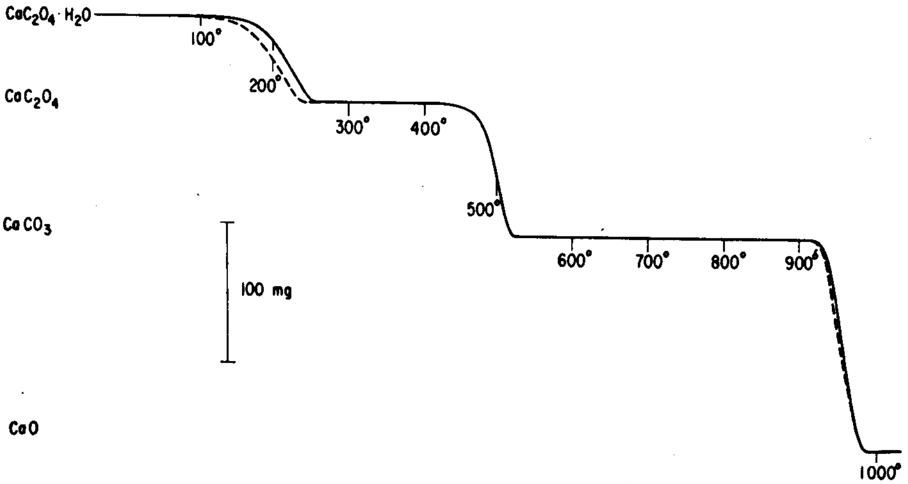


FIG. 9.—Effect of sample container upon thermogram for calcium oxalate monohydrate in flowing dry carbon dioxide (500 mg, 300 degree/hr):
– – – – quartz dish,
——— porcelain crucible.

solely the gas involved in the reaction. When the reversible pyrolysis of calcium carbonate was performed in a given container, the higher the pressure of carbon dioxide in the atmosphere, the higher the value of the procedural decomposition temperature and therefore, the smaller the reaction interval, ($T_f - T_i$). (Compare Fig. 9 with Figs. 5, 4, 6, and 10.)

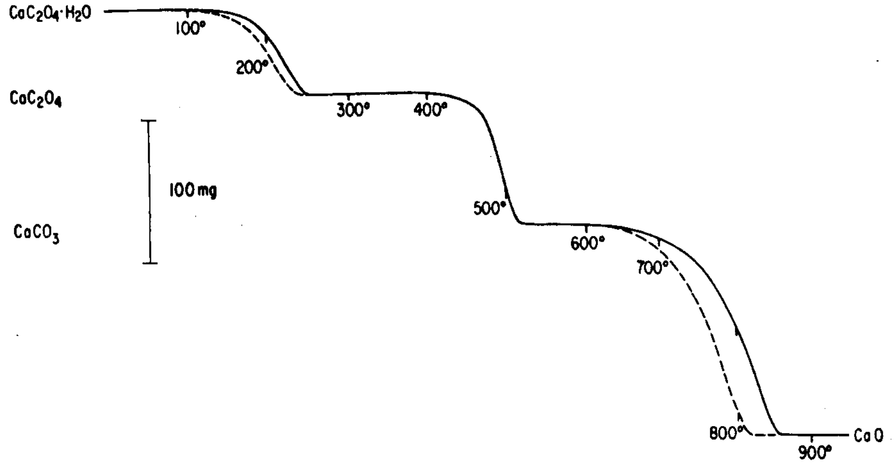


FIG. 10.—Effect of sample container upon thermogram for calcium oxalate monohydrate in flowing dry nitrogen (500 mg, 300 degree/hr):
– – – – quartz dish,
——— porcelain crucible.

When the pyrolysis was carried out in a flowing stream of dry nitrogen (Fig. 10), both the loss of water and the loss of carbon dioxide were affected by the shape of the container; the loss of carbon monoxide was unaffected. There is a thermodynamic possibility that the loss of carbon dioxide, illustrated by the dashed curve of Fig. 10, was caused by reaction between the calcium carbonate and the quartz dish. However, Longuet[59] has shown that this reaction becomes significant below 900° only if both the silica and the calcium carbonate are finely divided and intimately mixed. We have repeated the pyrolysis of Fig. 10 using a platinum-lined quartz dish, and the results were the same as those obtained with the unlined dish. Both curves shown in Fig. 10, therefore, represent only the thermal dissociation of calcium carbonate.

The marked effect of container shape that is illustrated in Figs. 9 and 10 provides evidence that a significant pressure of water vapour and carbon dioxide must have existed in the interior of the crucible during dissociation, even when the atmosphere that flowed over the crucible entered the thermobalance free from either water or carbon dioxide or both.

In the study of reversible reactions or of reactions in which a component of the atmosphere can react either with the original sample or with a solid or gaseous decomposition product, one must recognise the possible existence of such partial pressure gradients throughout a mass of powdered sample. These gradients can effect both the shape of thermogravimetric curves[31,51,52] and the magnitude of thermal effects that accompany the reactions.[30] They can be reduced by packing the powder loosely in a shallow dish,[16] by using crucibles with micro-porous[15,29] or macro-porous[1] walls, or by passing a controlled atmosphere through the bed of powdered sample. The effectiveness of the latter technique for differential thermal analysis has been vividly demonstrated by Stone,[50] who has also announced the development of thermogravimetric equipment to provide dynamic gas flow through the specimen under study.[46] Papailhau[39,40] has designed a crucible, for use with a null-type balance, that permits an externally generated atmosphere to be passed through the entire bed of powdered sample.

Except for the experiments of Figs. 9 and 10 that were made with a quartz dish, all differential thermal and thermogravimetric measurements described in this report were made with Coors high form-000 porcelain crucibles, in which both thermal gradients and partial pressure gradients undoubtedly existed. Reproducible results were obtained by careful control of experimental conditions, but, as illustrated by Fig. 10, these results would have been different with more efficient interaction between solid sample and gaseous atmosphere. The interpretation of the experiments has been made with this restriction in mind.

Comparison of dry nitrogen and dry oxygen

Thermograms that were obtained by heating calcium oxalate monohydrate in flowing atmospheres of dry nitrogen and of dry oxygen are shown in Fig. 11. The dehydration step is unaffected by the change in atmosphere, and the two curves are nearly identical in this region because both gases are equally effective in sweeping evolved water vapour away from the sample surface. On the other hand, the thermograms diverge at the intermediate stage because in oxygen or air the secondary oxidation of carbon monoxide raises the temperature of the unreacted solid at a rate greater than the heating rate of the furnace, producing a marked acceleration in the decomposition rate. The decomposition of calcium oxalate occurs more rapidly and is completed at a lower furnace temperature in an atmosphere of dry oxygen (or air) than in an atmosphere of dry nitrogen.

Although the product of this decomposition in either atmosphere is calcium carbonate, the procedural decomposition temperature for the subsequent loss of carbon dioxide was higher in the run made in an oxygen atmosphere than for that made in a nitrogen atmosphere (Fig. 11). This small difference is not an artifact of the instrument. Indeed, thermograms that we obtained by heating separate portions of the same sample of *calcium carbonate* in nitrogen and in air were identical in the region of weight loss because nitrogen and air were equally effective in sweeping away the evolved carbon dioxide. However, the calcium carbonate produced by the decomposition of a given sample of calcium oxalate in an oxygen atmosphere is *not* identical with that produced by decomposition of the same material in a nitrogen atmosphere.

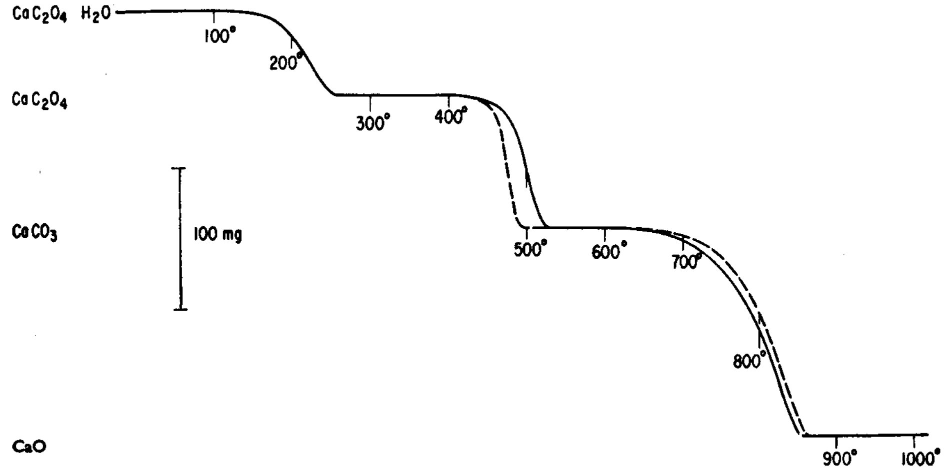


Fig. 11.—Effect of atmosphere upon thermogram for calcium oxalate monohydrate (500 mg, porcelain crucible, 300 degree/hr):
– – – – dry oxygen,
——— dry nitrogen.

The dry oxygen run shown in Fig. 11 was repeated, but at a temperature of about 450° the furnace was turned off and the flowing oxygen was replaced by flowing nitrogen. After the temperature had dropped to about 140°; the heating rate of 300 degree/hr was resumed. The resulting thermogram, although obtained in a nitrogen atmosphere, was identical above 500° with the dashed oxygen curve of Fig. 11. The thermogravimetric behaviour of the calcium carbonate in these experiments was determined by the atmosphere in which it had been formed and not by the atmosphere in which it was decomposed. Thermogravimetry cannot disclose whether this difference in pyrolytic behaviour is a reflection of differences in particle size, surface area, lattice imperfections, or some other characteristics, but these experiments and those shown in Fig. 10 do illustrate the usefulness of thermogravimetric measurements, made on a reliable balance, for quickly surveying a variety of experimental conditions and thus disclosing those areas in which more detailed studies should be made, possibly with other supplementary techniques. As will be shown later, the shape of even a single thermogram can indicate complexities in the reaction under study.

Sample weight

In the earlier discussion of successive, partially overlapping reactions, certain similarities were noted between the effects of heating rate and sample weight upon the shape of a dynamic thermogram. This parallelism cannot be carried too far. Unlike heating rate, sample weight is not a completely independent variable in thermogravimetry. For a given sample container a change in the weight of a powdered solid sample simultaneously changes the thickness of the sample bed, its total heat capacity, and its area of contact with the walls of the container, through which much of the heat transfer with the furnace atmosphere occurs.

Some of these factors can change during a pyrolysis, as illustrated by Fig. 12, in which are superimposed the thermograms obtained in ambient air with approximately 1 g of calcium oxalate monohydrate (Fig. 6) and those obtained with equivalent quantities of the anhydrous salt and calcium carbonate. The relationship between curve 12B and the second weight-loss section of curve 12A is the same as shown in Fig. 5 and arises from the overlap of the dehydration reaction and the loss of carbon monoxide. However, even though this second stage, the loss of carbon monoxide, was complete before the procedural decomposition temperature of calcium carbonate was reached (and therefore a true plateau was observed for this compound), the value of T_i for the loss of carbon dioxide is markedly lower for curve 12C than for curves 12A and B. Examination of the crucibles at the end of each pyrolysis showed that the residues of calcium oxide from runs 12A and B were more loosely packed than that from run 12C, and were separated by an air gap from the wall of the sample crucible. Although the final weight of calcium oxide was the same in each run, its volume represented a larger shrinkage from the initial sample volume in runs A and B than in run C. The gaps produced by this shrinkage undoubtedly reduced the flow of heat

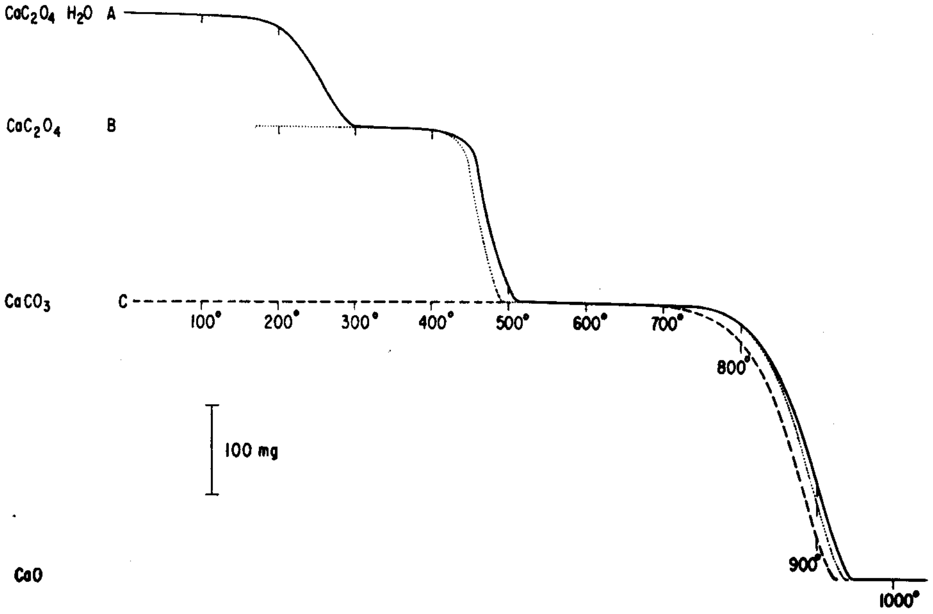


FIG. 12.—Thermogram for successive partially overlapping reactions (porcelain crucible, ambient air, 300 degree/hr; curve A as for Fig. 6):

——— 1·019 g of calcium oxalate monohydrate,
...... 0·893 g of calcium oxalate,
– – – – 0·699 g of calcium carbonate.

between the sample and furnace and thus contributed, at least in part, to the higher value of T_i in runs A and B.

Undoubtedly the effect of sample shrinkage observed with the 1-g (and equivalent) samples of Fig. 12 was also present during the runs made with 0·5-g (and equivalent) samples of Fig. 4, but because the sample was smaller the magnitude was much less.

Thus, although the thermograms of Fig. 4, demonstrate that under certain conditions the curve for a multi-stage pyrolysis can be considered as the exact summation of the curves for the individual stages, those of Figs. 11 and 12 emphasise that under other conditions the thermogravimetric behaviour of a given substance may depend upon whether it is the material initially loaded into the sample container or whether it is formed in the container by decomposition of a percursor.

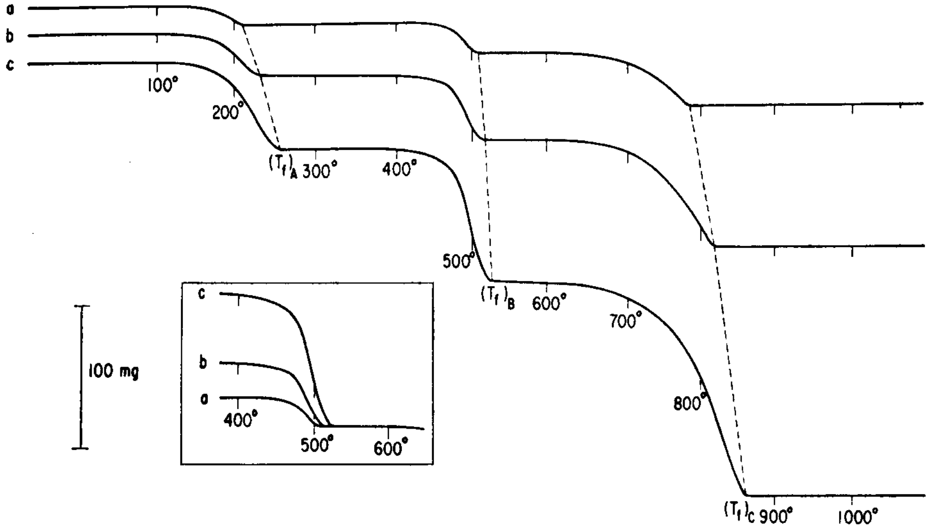


FIG. 13.—Effect of sample weight upon thermogram for calcium oxalate monohydrate in flowing dry nitrogen (porcelain crucible, 300 degree/hr):

a—126 mg of calcium oxalate monohydrate,
b—250 mg of calcium oxalate monohydrate,
c—500 mg of calcium oxalate monohydrate.

Insert shows three curves superimposed at calcium carbonate level to emphasise effect of sample weight on loss of carbon monoxide.

From the foregoing results it appears that no generalisations can be made about the effect of sample weight upon the procedural decomposition temperature, particularly for intermediate products. Even with powdered calcium carbonate as a starting material, Richer and Vallett[44,45] found that T_i was virtually independent of sample weight in the range 0·25 to 1 g, both in nitrogen and carbon dioxide. At 100 degree/hr, T_i was 517° in nitrogen and 914° in carbon dioxide. On the other hand, once the decomposition of a powdered solid has begun, it generally does not occur uniformly in every particle throughout the entire mass of sample.[31,51,52,55] Measurable temperature gradients exist even across relatively thin beds of powder.[32–34] Under such non-homogeneous conditions one would expect that the time required for complete decomposition of a powdered solid would increase with increase of sample weight. Because the furnace heating rate is linear there would be a resultant increase in the observed value of T_f. This expected increase was observed by Richer and

Vallet[44,45] for the pyrolysis of calcium carbonate and in this work for each stage in the pyrolysis of calcium oxalate monohydrate in nitrogen at 300 degree/hr (Fig. 13).

A perturbation in this generalisation can occur if the reaction is exothermic. The sample temperature then increases more rapidly than does the measured furnace temperature, and the resultant acceleration in specific reaction rate may compensate, at least in part, for the increase in sample weight. It has already been noted that in air the endothermic decomposition of calcium oxalate is accompanied by the highly exothermic oxidation of carbon monoxide, with a consequent acceleration of the reaction rate. As a result, as shown in Fig. 14, T_f for the decomposition of calcium oxalate in air is less than in nitrogen and is virtually independent of the starting weight of monohydrate, at least in the range 125 to 500 mg. A comparison between Figs. 14 and 6 shows the normally expected increase in T_f between 500 mg and 1 g and the pronounced increase in T_i for calcium carbonate that was noted in the discussion of Fig. 12.

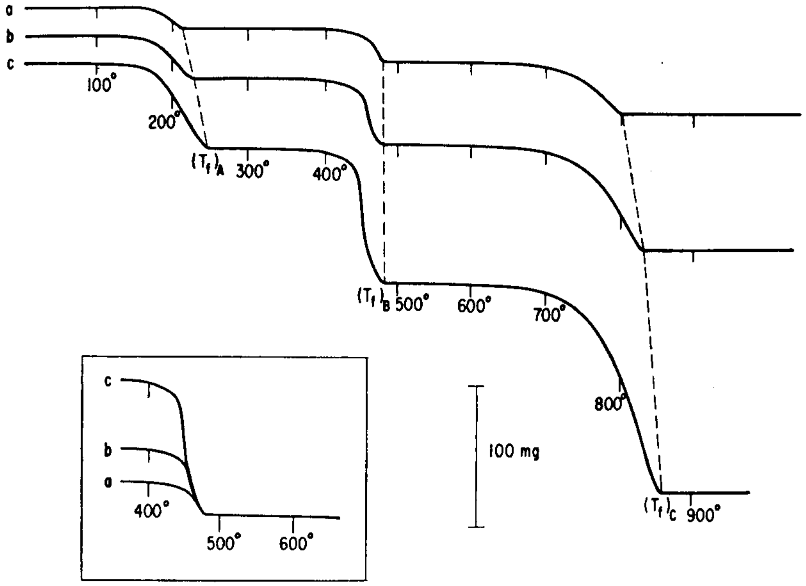


FIG. 14.—Effect of sample weight upon thermogram for calcium oxalate monohydrate in ambient air (porcelain crucible, 300 degree/hr):

a—126 mg of calcium oxalate monohydrate
b—250 mg of calcium oxalate monohydrate,
c—500 mg of calcium oxalate monohydrate.

Insert shows three curves superimposed at calcium carbonate level to emphasise that T_f for loss of carbon monoxide is independent of sample weight.

Water vapour

The value of a dynamic thermogram in the preliminary study of chemical reactions lies not just in its gross characteristics, such as plateaux or clearly marked changes of slope, from which one can draw inferences about the stoichiometry of the reaction, but also in the more subtle variations of shape that may reflect the complexity of the reactions that produce the more noticeable, over-all weight changes. This is illustrated by a re-examination of Fig. 4 for the pyrolysis of calcium oxalate monohydrate in ambient air. The over-all stoichiometry of the three distant stages is clearly defined by each of the plateaux. However, there is a significant qualitative difference between the shape of the curve that marks the loss of carbon monoxide and the shapes of the curves for the loss of water and of carbon dioxide. The latter curves are smooth and continuous between the two plateaux, but the loss of carbon monoxide is characterised by three rather abrupt changes in slope that have no apparent stoichiometric significance. This shape is reproducible and is not an artifact of the instrument, although it can be modified by using a platinum instead of a porcelain crucible. Clearly, the thermogram suggests that further investigation of this stage of the reaction is warranted.

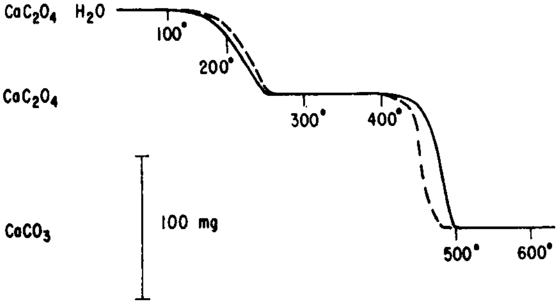


Fig. 15.—Effect of water vapour upon thermogram for calcium oxalate monohydrate in oxidising atmosphere (500 mg, porcelain crucible, 300 degree/hr):

——— dry air,
– – – – humid air.

In the region of carbon monoxide loss the curve obtained in ambient air (curve A of Fig. 4 and curve *c* of Fig. 14) is identical to the dashed curve in humid air.

Additional experiments were performed, which showed (Fig. 15) that the unusual shape, originally observed in ambient air, could be reproduced exactly in a flowing atmosphere of humidified air, but that in dry air the loss of carbon monoxide was characterised by the same smooth continuous shape noted in Fig. 11 for dry nitrogen and oxygen. Furthermore, the accelerating effect of water vapour upon the decomposition of CaC_2O_4 is clearly evident from the curves of Fig. 15. Finally, a comparison between thermograms obtained in dry air, dry nitrogen, and humid nitrogen (Fig. 16) shows that the loss of carbon monoxide begins more abruptly and at a lower furnace

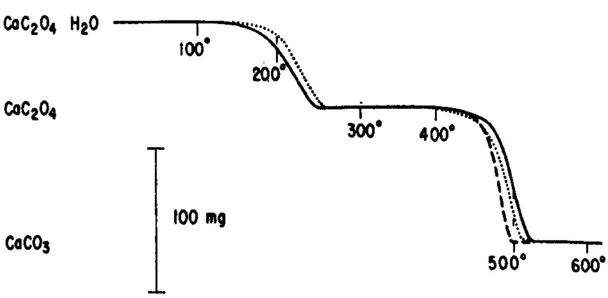


Fig. 16.—Effect of water vapour upon thermogram for calcium oxalate monohydrate in inert atmosphere (500 mg, porcelain crucible, 300 degree/hr):

——— dry nitrogen,
. . . . . . humid nitrogen,
– – – – dry air.

temperature in humid nitrogen than in dry air, although the total loss is completed at a lower furnace temperature in the latter gas.

That water vapour has a marked effect upon the decomposition of anhydrous calcium oxalate was confirmed by repeating the thermal experiments illustrated in Fig. 7 with humidified gases. The exotherm noted previously in dry oxygen was still present, but it had been shifted about 40° to a lower temperature. In humidified nitrogen, however, the magnitude of the endotherm for the oxalate decomposition was significantly reduced. The combustion train experiment was also repeated as a two-part experiment. During the first 3-hr period the carrier gas was humidified nitrogen; during the second 3-hr period it was dry oxygen. For the period in humidified nitrogen the combustion train was modified by inserting a large capacity water absorption tube at the exit end of the pyrolysis tube to ensure that no water vapour was present in the gas that entered the first Ascarite tube. In addition, an Anhydrone absorption tube was inserted in the train immediately after the copper oxide furnace. Any hydrogen in the gas stream leaving the reaction zone would be oxidised by the hot copper oxide and be absorbed as water in the Anhydrone tube.

The results are listed as runs 3(a) and 3(b) in Table II. The following comments are pertinent to the data:

1. The amount of calcium oxalate that decomposed during the first 3 hr at 420° was significantly greater in humid nitrogen than in dry nitrogen.

2. Unlike run 2 made in dry nitrogen, less than one-third of the total carbon dioxide that was absorbed by the Ascarite appeared in the tube that was mounted at the exit end of the copper oxide furnace, indicating that less than one-third of the evolved carbon monoxide left the reaction zone unchanged.

3. Part of the carbon monoxide evolved in the humidified nitrogen atmosphere was oxidised by the water vapour to carbon dioxide:

$$CO + H_2O = CO_2 + H_2 \qquad \Delta H_{700^\circ K} = -9{\cdot}1 \text{ kcal}^7 \qquad (6)$$

The hydrogen that was simultaneously produced appeared as water after it had passed through the copper oxide furnace.

4. Not all of the evolved carbon monoxide ended up as carbon dioxide. Unlike runs made in dry air and dry nitrogen, the total mole of carbon dioxide absorbed during run 3(a) was significantly less than the weight loss of the sample, calculated as mole of carbon monoxide. During this run in humid nitrogen a yellow deposit appeared at the cool exit end of the combustion tube. Preliminary pyrolysis experiments in humid nitrogen with both calcium and magnesium oxalates had produced similar deposits, which were soluble in benzene and whose infrared spectra showed them to contain aliphatic C-H bonds. In addition to hydrogen, various hydrocarbon species are thermodynamically possible products of the reaction between carbon monoxide and water vapour. Depending upon their volatility, such species can condense out of the gas stream at various points in the train before the copper oxide furnace and therefore would not appear ultimately as carbon dioxide and water. More volatile hydrocarbons might reach the hot copper oxide tube but be incompletely oxidised in passing through it. Experience in this Laboratory has shown that at the recommended temperature of 700° for operation of the copper oxide furnace, even the oxidation of methane may be slow enough to permit small amounts of the gas to pass

through the reaction zone unchanged. For the foregoing reasons a reliable material balance was not possible in this experiment.

5. To confirm the reliable operation of the train itself, run 3(b) was made by passing dry oxygen over the residue remaining from 3(a). As seen from the results in Table II, all of the evolved carbon monoxide was oxidised in the reaction zone and was absorbed as carbon dioxide in the first Ascarite tube.

No further work has been performed to explore and understand the effect of water vapour upon this reaction, and certainly thermogravimetry alone will not provide the answers. Thermogravimetry has provided, however, as few other techniques could, simple and graphic evidence for the existence of an effect that might warrant further investigation.

CONCLUSION

Calcium oxalate monohydrate is ideally suited for demonstrating many of the factors that affect the quality of thermogravimetric measurements. It is particularly useful for showing the great variety of effects that may be produced by three common atmospheric constituents, carbon dioxide, oxygen and water vapour, as well as three common experimental variables, heating rate, shape of sample container and size of sample. These variables and the interaction between them will determine whether the thermogravimetric curve for the pyrolysis of calcium oxalate monohydrate will appear as a succession of independent reactions or as a sequence of partially overlapping and non-independent reactions. Calcium oxalate monohydrate can be used as a standard for judging the performance of a thermobalance only if it is pyrolysed under carefully controlled conditions.

Acknowledgments—The authors acknowledge the skilful assistance of Adrian Breitenstein, Harley W. Middleton and Mrs. Renette Vincelette, in performing some of the measurements described in this report. They are also indebted to Dr. Paul D. Garn, University of Akron, for suggesting both the interpretation of the calcium carbonate portion of Fig. 11 and the revised experiments described in the text.

Zusammenfassung—Die Pyrolyse von Calciumoxalat-Monohydrat an Luft nimmt in der Literatur über Thermogravimetrie einen hervorragenden Platz ein. Ein Thermogramm dieser Reaktion war die erste von Duval und Mitarbeitern publizierte Pyrolysenkurve und Duval und andere schlugen diese Substanz als Bezugssubstanz zur Beurteilung der Anzeige einer Thermowaage vor. Die Pyrolyse von Calciumoxalat-Monohydrat gibt aber unter verschiedenen Bedingungen beträchtliche Unterschiede in den Thermogrammen. Die Einflüsse von Probengröße, Aufheizgeschwindigkeit, Atmosphäre und Gefäßgeometrie werden in einer Reihe von Thermogrammpaaren vorgelegt und die Unterschiede mit zusätzlichen Informationen aus Differential thermoanalyse und Versuchen im Verbrennungs-schiffchen erklärt. Besonders wichtig sind Änderungen der Atmosphäre: untersucht wurden trockener und feuchter Stickstoff, trockene und feuchte Luft, trockener Sauerstoff, Kohlendioxyd und Kohlenmonoxyd. Selbst geringfügige Änderungen der Form eines Thermogramms von einer verläßlichen Waage können die Kompliziertheit der Reaktionen widerspiegeln, die die leichter bemerkbaren Gewichtsänderungen insgesamt hervorrufen. Die hier vorgelegten Ergebnisse grenzen auf diese Weise die Arbeitsbedingungen ab, unter denen Calciumoxzlat-Monohydrat als thermogravimetrische Bezugssubstanz verwendet werden kann, und sie zeigen, daß sein Verhalten in einer Thermowaage unter kontrollierten Bedingungen eine ungewöhnlich vielseitige Anleitun zur Interpretation thermogravimetrischer Messungen bieten kann.

Résumé—La pyrolyse dans l'air de l'oxalate de calcium monohydraté occupe une place unique dans la littérature de la thermogravimétrie. Non seulement la première courbe de pyrolyse publiée par Duval et ses collaborateurs a été un thermogramme de cette réaction, mais Duval et d'autres auteurs ont proposé ce composé comme substance de référence pour juger des possibilités d'une thermobalance. Toutefois, la pyrolyse de l'oxalate de calcium monohydraté dans des conditions variées conduit à des différences considérables dans les thermogrammes. Les influences de la taille de la prise d'essai, de la vitesse de chauffage, de l'atmosphère, et de la forme du récipient, sont présentées dans une série de thermogrammes comparatifs, et les différences sont confirmées au moyen de preuves supplementaires apportées par l'analyse thermique différentielle et des expériences de combustion en série. Des variations dans l'atmosphère sont particulièrement importantes, et les atmosphères étudiées sont l'azote sec, l'azote humide, l'air sec, l'air humide, l'oxygène sec, le gaz carbonique sec et l'oxyde de carbone sec. Même de très faibles variations dans la forme d'un thermogramme obtenu avec une balance fidèle peuvent refléter la complexité des réactions qui produisent les changements de poids globaux les plus remarquables. Les résultats présentés dans ce mémoire délimitent ainsi les conditions d'emploi de l'oxalate de calcium monohydraté comme substance de référence thermogravimétrique, et montrent que son comportement dans une thermobalance, dans des conditions contrôlées, peut constituer un exemple particulièrement souple pour l'interprétation des mesures thermogravimétriques.

REFERENCES

[1] M. Bachelet and M. Christen, *Compt. rend.*, 1960, **251**, 2961.
[2] C. Barcia Goyanes, *Inform. Quim. Anal.* (*Madrid*), 1955, **9**, 159.
[3] G. G. Briggs, U.S. At. Energy Comm., NLCO-720, 1958.
[4] M. Capestan, *Ann. Chim.* (*France*), 1960, **5**, 207.
[5] P. Caro and J. Loriers, *J. Rech. Centre Nat. Rech. Sci., Lab. Bellevue* (*Paris*), 1957, **39**, 107.
[6] B. Claudel, M. Perrin and Y. Trambouze, *Compt. rend.*, 1961, **252**, 107.
[7] J. P. Coughlin, *U.S. Bur. Mines Bull.*, 1954, 542.
[8] J. Cueilleron and O. Hartmanshenn, *Bull. Soc. Chim. France*, 1959, 172.
[9] R. W. M. D'Eye and P. G. Sellman, *J. Inorg. Nuclear Chem.*, 1955, **1**, 143.
[10] C. D. Doyle, *Analyt. Chem.*, 1961, **33**, 77.
[11] P. Dubois, *Bull. Soc. Chim. France*, 1936, **3**, 1178.
[12] C. Duval, *Analyt. Chem.*, 1951, **23**, 1271.
[13] *Idem*, *Inorganic Thermogravimetric Analysis.* Elsevier Publishing Co., Amsterdam, 1953.
[14] L. Erdey and F. Paulik, *Acta Chim. Acad. Sci. Hung.*, 1955, **7**, 27.
[15] J. L. Evans and J. White, *The Thermal Decomposition* (*Dehydroxylation*) *of Clays* in *Kinetics of High Temperature Processes*, W. D. Kingery, ed. Technology Press of MIT, Cambridge, 1959, pp. 301–8.
[16] P. D. Garn and J. E. Kessler, *Analyt. Chem.*, 1960, **32**, 1900.
[17] A. Glasner and M. Steinberg, *J. Inorg. Nuclear Chem.*, 1961, **16**, 279.
[18] *Idem*, *ibid.*, 1961, **22**, 39.
[19] *Idem*, *ibid.*, 1961, **22**, 156.
[20] H. Guérin, J. Masson, P. Mattrat, R. Boulitrop, C. Duc-Maugé, R. Martin and R. Mas, *Bull. Soc. Chim. France*, 1953, 440.
[21] H. Guérin, *ibid.*, 1955, 1536.
[22] M. Guichard, *ibid.*, 1935, **2**, 539.
[23] *Idem*, *Ann. Chim.* (*France*), 1938, **9**, 323.
[24] G. Guiochon, *Chimie et Industrie*, 1960, **84**, 734.
[25] *Idem*, *Analyt. Chem.*, 1961, **33**, 1124.
[26] P. L. Günther and H. Rehaag, *Ber.*, 1938, **71**, 1771.
[27] J. Haladjian and G. Carpenti, *Bull. Soc. Chim. France*, 1956, 1679.
[28] K. J. Hill and E. R. S. Winter, *J. Phys. Chem.*, 1956, **60**, 1361.
[29] H. E. Kissinger, H. F. McMurdie and B. S. Simpson, *J. Amer. Ceram. Soc.*, 1956, **39**, 168.
[30] D. Kolar, E. D. Lynch and J. H. Handwerk, *ibid.*, 1962, **45**, 141.
[31] R. Marcellini, thesis, Faculté des Sciences de Lyon, 1959.
[32] H. Mauras, *Bull. Soc. Chim. France*, 1954, 762.

[33] *Idem, ibid.*, 1959, 16.
[34] *Idem, ibid.*, 1960, 260.
[35] P. Murray and J. White, *Trans. Brit. Ceram. Soc.*, 1949, **48**, 187.
[36] A. E. Newkirk, *Analyt. Chem.*, 1960, **32**, 1558.
[37] K. J. Notz, U.S. At. Energy Comm., NLCO-814, 1960.
[38] V. M. Padmanabhan, S. C. Saraiya and A. K. Sundaram, *J. Inorg. Nuclear Chem.*, 1960, **12**, 356.
[39] J. Papailhau, Brevet D'Invention, N. Provisoire PV763, 520 (4/18/58).
[40] *Idem, Bull. Soc. Franc. Mineral. Crist.*, 1959, **82**, 367.
[41] F. Paulik, J. Paulik and L. Erdey, *Acta Chim. Acad. Sci. Hung.*, 1961, **26**, 143.
[42] S. Peltier and C. Duval, *Analyt. Chim. Acta*, 1947, **1**, 345.
[43] H. Peters and H. Wiedemann, *Z. Anorg. Chem.*, 1959, **300**, 142.
[44] A. Richer and P. Vallet, *Bull. Soc. Chim. France*, 1953, 148.
[45] A. Richer, Inst. Recherches de la Sidérugie, Ser, A, No. 187, 1960.
[46] Robert L. Stone Co., Austin, Texas, Model TGA-2, 1962.
[47] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffee, *Nat. Bur. Std.* (*U.S.*) *Circ.*, **500**, 1952.
[48] E. L. Simons, A. E. Newkirk and I. Aliferis, *Analyt. Chem.*, 1957, **29**, 48.
[49] J. R. Soulen and I. Mockrin, *ibid.*, 1961, **33**, 1909.
[50] R. L. Stone, *ibid.*, 1960, **32**, 1582.
[51] S. J. Teichner, R. P. Marcellini and P. Rue, *Adv. Catalysis*, 1957, **9**, 458.
[52] S. J. Teichner, J. Aigueperse, B. Arghlropoulos and R. P. Marcellini, 1959 *XVII Intern. Congr. Pure Appl. Chem., Munich, Abstracts*, **1**, 207.
[53] P. Vallet, *Bull. Soc. Chim. France*, 1936, **3**, 103.
[54] P. Vallet and M. Bassière, *ibid.*, 1938, **5**, 546.
[55] P. Vallet and A. Richer, *Compt. rend.*, 1954, **238**, 1020.
[56] W. W. Wendlandt, *J. Chem. Educ.*, 1961, **38**, 571.
[57] C. L. Wilson, *J. Roy. Inst. Chem.*, 1959, **83**, 550.
[58] L. Wöhler and W. Schuff, *Z. anorg. Chem.*, 1932, **209**, 57.
[59] P. Longuet, *Rev. materiaux construit, et trav. publ. C*, No. **537**,139; No. **538–539**, 183; No. **540**, 233 (1960); *Bull. soc. franc. ceram.*, No. 48, 69 (1960).

Talanta, 1964, Vol. 11, pp. 573 to 579. Pergamon Press Ltd. Printed in Northern Ireland

COLORIMETRIC DETERMINATION OF NICKEL WITH 2-MERCAPTOBENZOTHIAZOLE

E. G. WALLICZEK
Rhoanglo Mine Services Limited
Research and Development Division
P.O. Box 172, Kitwe, N. Rhodesia

(*Received* 1 *September* 1963. *Accepted* 24 *October* 1963)

Summary—A colorimetric method has been developed for determining nickel with 2-mercaptobenzothiazole. At pH 7·7–8·1 in an ammoniacal medium nickel forms a yellow-brown complex, insoluble in water but soluble in chloroform. It is suitable for determining nickel in the concentration range 0·4–16 ppm with an average error of 0·5–2%. Cobalt, copper and iron interfere and have to be removed by an anion-exchange method before analysis. Bismuth and lead, if present, are removed with hydrogen sulphide, and complex formation of 2-mercaptobenzothiazole with alkali metals is prevented by fluoridation. No other metals were found to interfere.

THIS paper describes an investigation of 2-mercaptobenzothiazole as a colorimetric reagent in chloroform for the determination of nickel. In procedures involving the use of dimethylglyoxime,[1] manganese interferes and has to be removed before the colorimetric determination can be applied. A literature survey revealed that 2-mercaptobenzothiazole has not been reported previously for the colorimetric determination of nickel.

2-Mercaptobenzothiazole is not specific for nickel, but the reagent allows the determination of nickel in the presence of many other metal ions. It has already found use as a reagent for the gravimetric determination of a variety of metals too numerous to be listed here. Majumdar and Chakrabartty[2] have also investigated this reagent for the colorimetric determination of palladium.

EXPERIMENTAL

Reagents

2-Mercaptobenzothiazole. 1% w/v in chloroform; for purification of the commercial material see *Appendix.*

Standard nickel solution. A stock solution prepared from *Specpure* nickel sponge was suitably diluted, so that 1 ml contained 0·1 mg of nickel.

Hydrochloric acid. 0·5*M* solution prepared from A.R. reagent (Merck).

Aqueous ammonia. 0·5*M* solution prepared from A.R. reagent.

Hydrofluoric acid. Conc. (A.R.) and (1 + 20) solution prepared from A.R. reagent.

Chloroform. A.R.

Apparatus

Spekker absorptiometer (mercury vapour lamp), 2-cm and 4-cm cells and Hilger No. 1 violet-blue filters.

Procedure

Transfer 1·0, 2·0, 3·0 and 8·0-ml portions of the standard nickel solution from a micro burette into a series of beakers containing 10 ml of distilled water. Using a pH meter, adjust the pH of the solutions to 7·7–8·1 with 0·5*M* aqueous ammonia or 0·5*M* hydrochloric acid. Transfer the solutions quantitatively into 100-ml separating funnels and extract the nickel with 2 × 10 and 1 × 5 ml of

1 % 2-mercaptobenzothiazole in chloroform. Shake gently for 2 min for each extraction and filter the organic phase into a 50-ml volumetric flask by means of a small funnel fitted with a cotton wool plug. After filtration, wash the cotton plug through with fresh chloroform and make the extracts up to the mark with chloroform. Measure the optical density of the yellow-brown solutions against a blank in chloroform using 2-cm cells. Plot a graph relating the optical density to the quantity of nickel present; it should be linear and pass through the origin.

Calibrations containing from 0·01–0·10 mg of nickel should be carried out in the same way but using 25-ml volumetric flasks and 4-cm cells. Extraction of nickel is established with 10 ml and 5 ml of 1 % 2-mercaptobenzothiazole in chloroform.

DISCUSSION

The nickel-2-mercaptobenzothiazole complex in chloroform is yellow-brown whereas the reagent solution itself is almost colourless. The absorption spectrum for the coloured complex shows a maximum near 750 mμ.

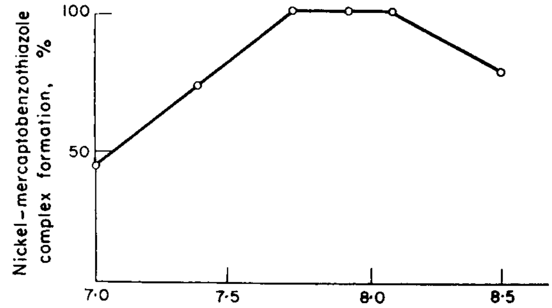


FIG. 1.—Complex formation as a function of pH.

The complex formation is dependant on the pH of the aqueous solution and Fig. 1 indicates that a pH of 7·7–8·1 is critical for the quantitative formation of nickel-2-mercaptobenzothiazole. The optical density of the complex in chloroform showed no change after 24 hr.

Job's method of continuous variations[3] shows that every atom of nickel in the complex is bound to two molecules of 2-mercaptobenzothiazole and that a single complex species is formed in solution.

Various metal ions have been tested, after fluoridation, by the method described and their colour reactions are as follows:

Bi: yellow; Co: green; Cu: yellow; Fe: brown;
Ni: yellow-brown; Pb: yellow; Pd not tested.

Al, Ag, Au, Ba, Be, Ca, Cd, Ce, Cr, Hg, K, Li, Mg,
Mo, Mn, Na, Re, Se, Sr, Sn, Te, Ti, U, Zr, Zn:
no colour reaction

The interference from cobalt, copper, bismuth and iron is entirely removed by an anion exchange method* on a large column with a resin bed of 350-ml volume,† rejecting the first 100 ml of eluate, after which 500 ml are collected for the analysis of nickel in 8*M* hydrochloric acid as described by Liberman.[4] Lead, if present, passes

---

* Permutit "De-Acidite" FF(SRA 65) anion-exchange resin, chloride form, 14–52 mesh.

† At the discretion of the analyst the size of the column may, of course, be adjusted in accordance with the size of the sample.

through the column but is removed by gassing with hydrogen sulphide for a period of 5 min at pH 1 either before or after the anion-exchange separation.

After removal of all interfering metal ions the hydrochloric acid eluate is evaporated and made up to a convenient volume. An aliquot which should contain 0·02–0·8 mg of nickel is pipetted into a platinum crucible and 2 drops of sulphuric acid added, followed by 1 ml of perchloric acid. The sample is evaporated to dryness preferably on a sand bath. After cooling, 0·5 ml of hydrofluoric is added and the sample is again evaporated to dryness. The sample residue in the platinum crucible is dissolved by the addition of 3·0 ml of (1 + 20) hydrofluoric acid whilst heating. The sample solution is transferred into a beaker and the pH adjusted to 7·7–8·1, then quantitatively transferred into a 100-ml separating funnel and analysed as described. The concentration of nickel in the sample is read from the calibration curve.

RESULTS

To verify the method, tests were carried out in which known amounts of nickel were added to synthetic solutions of various metal ions. The results obtained are shown in Tables I–V.

TABLE I.—SOLUTIONS ALL EVENTUALLY MADE TO 50 ml IN CHLOROFORM. ERROR IS THE DIFFERENCE BETWEEN THE 'EXPECTED' AND 'OBSERVED' NICKEL CONCENTRATIONS EXPRESSED AS A PERCENTAGE.

(A) A 50-ml aliquot was separated on the column. After evaporation of the hydrochloric acid eluate the volume was adjusted to 100 ml and 5-ml portions were taken for each analysis.

Absorbance	Ni found, *mg*	Error
0·448	0·498	−0·5
0·450	0·500	0·0
0·450	0·500	0·0
0·445	0·496	−1·0
	Average:	−0·39

Co 25; Cu 5; Mn 2; Al 2; Na 1; K 1; Ca 1; Ni 0·20 g/l. Polarographic check on Ni: 0·19, 0·18, 0·20 g/l.

(B) A 10-ml aliquot was separated and the volume adjusted to 100 ml; 20-ml portions were taken for each analysis.

Absorbance	Ni found, *mg*	Error
0·360	0·400	0·0
0·335	0·396	−1·0
0·335	0·396	−1·0
	Average:	−0·70

Co 25; Cu 5; Mn 2; Al 2; Fe 2; Ni 0·02 g/l.

TABLE I (contd.)

Direct Determination of Nickel in Manganese Solution

(C) A 50-ml aliquot was taken for each analysis.

Absorbance	Ni found, *mg*	Error
0·448	0·498	−1·0
0·450	0·500	0·0
0·445	0·493	−2·0
	Average:	−1·0

Mn 30: Ni 0·01 g/l.

(D) A 2-ml aliquot was diluted to 100 ml and 20-ml portions were taken for each analysis.

Absorbance	Ni found, *mg*	Error
0·273	0·304	−2·0
0·280	0·312	0·0
0·275	0·308	−1·3
	Average:	−1·1

Mn 5; Ni 0·78 g/l.

(E) A 10-ml aliquot was made up to 100 ml and 10-ml portions were taken for each analysis.

Absorbance	Ni found, *mg*	Error
0·345	0·385	−1·3
0·348	0·388	−0·6
0·350	0·390	0·0
	Average:	−0·6

Co 50; Mn 2; Ni 0·39 g/l.

TABLE II.—DETERMINATION OF NICKEL IN MILD STEEL (SAMPLES FROM MILD STEEL RESIDUAL SERIES OF BUREAU OF ANALYSED SAMPLES LTD., NEWHAM HALL, MIDDLESBOROUGH, ENGLAND). ERROR IS THE DIFFERENCE BETWEEN THE 'EXPECTED' AND 'OBSERVED' NICKEL CONCENTRATIONS EXPRESSED AS A PERCENTAGE

(A) Sample SS 11 (solutions made to 50 ml in chloroform)

Wt. of sample, *g*	Absorbance	Ni found, *mg*	Error
1·5887	0·145	0·160	+1·0
1·4852	0·135	0·150	+1·0
1·1239	0·105		+2·0
		Average:	+1·3

Ni 0·01; Cr 0·04; Mo 0·19; Cu 0·01; W 0·01; Co 0·01; Sn 0·11; V 0·005; Al 0·008; Zr 0·045; Pb 0·003; Ti 0·002%.

TABLE II (contd.)

(B) Sample SS 12 (solutions made to 50 ml in chloroform)

Wt. of sample, *g*	Absorbance	Ni found, *mg*	Error
1·1124	0·295	0·330	−1·0
1·3765	0·375	0·415	+1·0
0·7840	0.210	0·235	0·0
		Average:	0·0

Ni 0·03; Cr 0·02; Mo 0·17; Cu 0·01; W 0·01; Co 0·25; Sn 0·02; V 0·01; Al 0·006; Zr 0·031; Mg 0·003; Pb 0·004; Ti 0·013%.

(C) Sample SS 17 (The sample was made up to a volume of 25 ml; 1·0, 5·0 and 10·0-ml portions were taken for analysis; sample weight: 0·7634 g; solutions eventually made to 50 ml in chloroform, except last solution made to 25 ml*)

Wt. of sample in aliquot	Absorbance	Ni found, *mg*	Error
0·1527	0·310	0·346	−1·3
0·1527	0·305	0·340	−3·0
0·3054	0·660	0·738	+4·3
0·03054*	0·29	0·068	−4·3
		Average:	−1·1

Ni 0·23; Cr 0·03; Mo 0·01; Cu 0·10; W 0·12; Co 0·12; Sn 0·005; V 0·10; Al 0·01; Zr 0·02; Pb 0·015; Ti 0·029%.

TABLE III.—NICKEL CONTENT IN COBALT ELECTROLYTE SOLUTIONS

(A) Group II metals were gassed with hydrogen sulphide at pH 1–2 for a period of 5 min. After filtration of the samples through Whatman No. 31 filter paper they were evaporated to near dryness, dissolved in 8*M* hydrochloric acid and column separated. Aliquots of 25 ml were taken from each sample. They were made up to a volume of 50 ml and 5-ml portions were taken for analysis. Solutions were all eventually made up to 50 ml in chloroform.

Sample No.	Absorbance	Ni found, *mg*
1	0·395	0·44
2	0·396	0·45
3	0·41	0·458
4	0·50	0·558

(B) Samples 1–4 were repeated but gassing with hydrogen sulphide was undertaken after the column separation.

Sample No.	Absorbance	Ni found, *mg*
1	0·395	0·440
2	0·400	0·455
3	0·410	0·460
4	0·520	0·570

Co 30; Mn 0·01; Cu 2 g/l.
Samples 2 and 4 contained 1 g of Bi/l.

TABLE IV.—DETERMINATION OF NICKEL IN LEACH RESIDUES

Samples of 2 g were digested in nitric and hydrochloric acid, evaporated to dryness, dissolved in 8*M* hydrochloric acid and column separated. The eluate, after evaporation, was gassed with hydrogen sulphide at pH 1–2. The samples were made up to a volume of 50 ml and 10-ml portions were taken for analysis. Solutions were all eventually made to 25 ml in chloroform.

Sample No.	Absorbance	Ni found, *mg*
5[a]	0·200	0·047
	0·200	0·047
	0·200	0·047
6[b]	0·140	0·028
	0·140	0·028
	0·140	0·028

[a] Dimethylglyoxime method after removal of Mn = 0·010% Ni. Mn 0·10; Bi 0·02; Cu 1·0; Co 0·4; Fe 17% (Al, Ca, Mg, Si rest).

[b] Dimethylglyoxime method after removal of Mn = 0·007% Ni. Mn 0·10; Bi 0·02; Cu 1·0; Co 0·3; Fe 16% (Al, Ca, Mg, Si rest).

TABLE V.—DETERMINATION OF NICKEL IN COBALT METAL IN THE PRESENCE OF MANGANESE (SAMPLES MADE UP TO VOLUME OF 100 ml AND EVENTUALLY MADE TO 50 ml IN CHLOROFORM)

Wt. of sample, *g*	Aliquot, *ml*	Absorbance	Ni found, *mg*
4·1717[a]	5	0·438	0·488
0·9290[a]	20	0·365	0·410
0·6230	20	0·250	0·280

[a] Because of the high cobalt load the eluate was evaporated and reintroduced on a fresh column for the removal of cobalt.

APPENDIX

Purification of 2-mercaptobenzothiazole

2-Mercaptobenzothiazole, when pure, is a creamy-white crystalline powder with a melting point of 182·2°. The reagent is available commercially but further purification is necessary.

Dissolve 20 g of commercial 2-mercaptobenzothiazole in 100 ml of 5% sodium hydroxide solution. Add 20 g of activated charcoal powder and shake for 5 min. Filter the solution under vacuum through a Buchner funnel using Whatman No. 42 filter paper. To the filtrate add 50 ml of 1% magnesium chloride (A.R.) solution and dilute to an approximate volume of 2 litres. Precipitate sodium 2-mercaptobenzothiazole whilst stirring with an excess of a dilute hydrochloric acid solution. Filter the precipitate under vacuum. Repeat the above operation without the use of charcoal or magnesium chloride. Filter and wash the precipitate freely with distilled water. Dissolve the partially dry filter cake in 200–300 ml of A.R. acetone. Filter the acetone solution, under vacuum, through a column approximately (0·5 inch in diameter) which contains 10 inches of Whatman cellulose powder. On top of the cellulose powder is placed a 3 to 4-inch layer of activated charcoal powder. The column packing is changed when half of the acetone solution has passed through it. Receive the filtrate into a 1-litre Buchner flask which contains 500 ml of distilled water. Filter the purified crystalline 2-mercaptobenzothiazole through a clean No. 3 Gooch crucible and dry the powder under vacuum over sulphuric acid.

Zusammenfassung—Eine quantitative Farbenmethode wurde für die Bestimmung von Nickel mit 2-Mercaptobenzothiazole im Bereich von 0·4–16 p.p.m. und einer Genauigkeit von 0·5–2 percent ausgearbeitet. Der Nickel 2-Mercaptobenzothiazole Komplex wird mit Chloroform in einem ammoniakalischem medium extrahiert und ist kritisch im pH Bereich 7·7–8·1. Kobalt, Kupfer und Eisen stören in der Bestimmung und werden mit einem Anionvertauscher in 8N Salzsäure festgehalten. Wismuth und Blei stören auch und müssen durch ausgasen mit Schwefelwasserstoff bei pH 1 zuvor oder nach der Anionvertauschtrennung beseitigt werden. Keine anderen Metalle stören.

Résumé—On a développé une méthode quantitative colorimetrique pour le dosage de nickel avec 2-mercaptobenzothiazole dans la portée de 0·4–16 p.p.m. avec une precision de 0·5–2 pourcent. Le complexe coloré du nickel 2-mercaptobenzothiazole est extrait avec du chloroforme dans un agent ammoniacal et est critique á pH 7·7–8·1 On élimine l'intervention du cobalt, du cuivre, et du fer par une methode d'échange dans du 8N acide chlorhydrique. Le bismuth et le plomb interférent aussi mais on les enléve par le moyen de passage au gaz avec du hydrogéne sulphuré á pH 1 on avant on aprés la séparation par l'échange du anion. On constata qu'aucun autre métal n'interféra.

REFERENCES

[1] F. Feigl, *Ber.*, 1924, **57**, 758.
[2] A. K. Majumdar and M. M. Chakrabartty, *Analyt. Chim. Acta*, 1959, **20**, 379.
[3] P. Job, *Ann. Chim.* (*France*), 1928, **9**, 113.
[4] A. Liberman, *Analyst*, 1955, **80**, 595.

Talanta, 1964 Vol. 11, pp. 581 to 592. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF GASES IN METALS BY AN IMPROVED VACUUM FUSION METHOD

TAKAYUKI SOMIYA, SHIZO HIRANO, HITOSHI KAMADA and IICHI OGAHARA
Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo,
1, Hongo-Motofuji, Tokyo, Japan

(*Received* 10 *September* 1963. *Accepted* 25 *October* 1963)

Summary—An improved gas extraction, collection, pressure measurement and calculation apparatus is described for use in the vacuum fusion method. It is designed for routine analysis and versatility in research investigations. The time required for gas collection is 1–2 min, including 15–60 sec for gas extraction. The total time required for a complete analysis is 7–9 min. The operating blank is 0·01–0·03 ml/30 min at 1850°. Analysis of 20 or more samples can be made in 8 hr, including loading, outgassing and gas analysis. A description is given of a newly designed gas extraction recording system for studying the optimum conditions for determination of gases in metals of current interest.

INTRODUCTION

IN recent years there has been an increasing demand for simple and rapid analytical methods that may be used under plant conditions for the determination of gases in metals and many such techniques have been successfully developed.[1–4] Particularly in the steel industry, more rapid and simple procedures have been required, and for the newer metals, such as titanium, uranium, hafnium, tantalum, *etc.*, more exacting demands are imposed on the analytical method.[5–8]

In this paper an improved vacuum fusion apparatus is described. The apparatus provides the following features:

1. A rapid gas extraction system.
2. A furnace assembly which is available for various kinds of sample and a wide range of sample weights.
3. A system in which the state of gas extraction can be simply and rapidly observed.
4. A simple and automatic pressure measurement system and minimisation of the use of mercury.
5. An automatic computer geared to the gas analysis system.

EXPERIMENTAL

Apparatus

The general appearance of the apparatus and the arrangement of the components are shown in Fig. 1. This apparatus differs from others which have been described in the fast gas extraction system, gas extraction recording system, gas collecting system and pressure measurement system. Some general considerations on these matters precede the detailed description of the various parts of the apparatus.

Gas extraction system

It is important that the gases evolved from a sample are removed from the furnace tube as rapidly as possible to minimise losses from chemisorption and reactions with evaporating metal vapours or evaporated metal films. This requirement has been met by connecting a newly designed, fast mercury diffusion pump[9] to the furnace tube by a wide-bore spherical joint (50-mm dia.) as shown in Fig. 4.

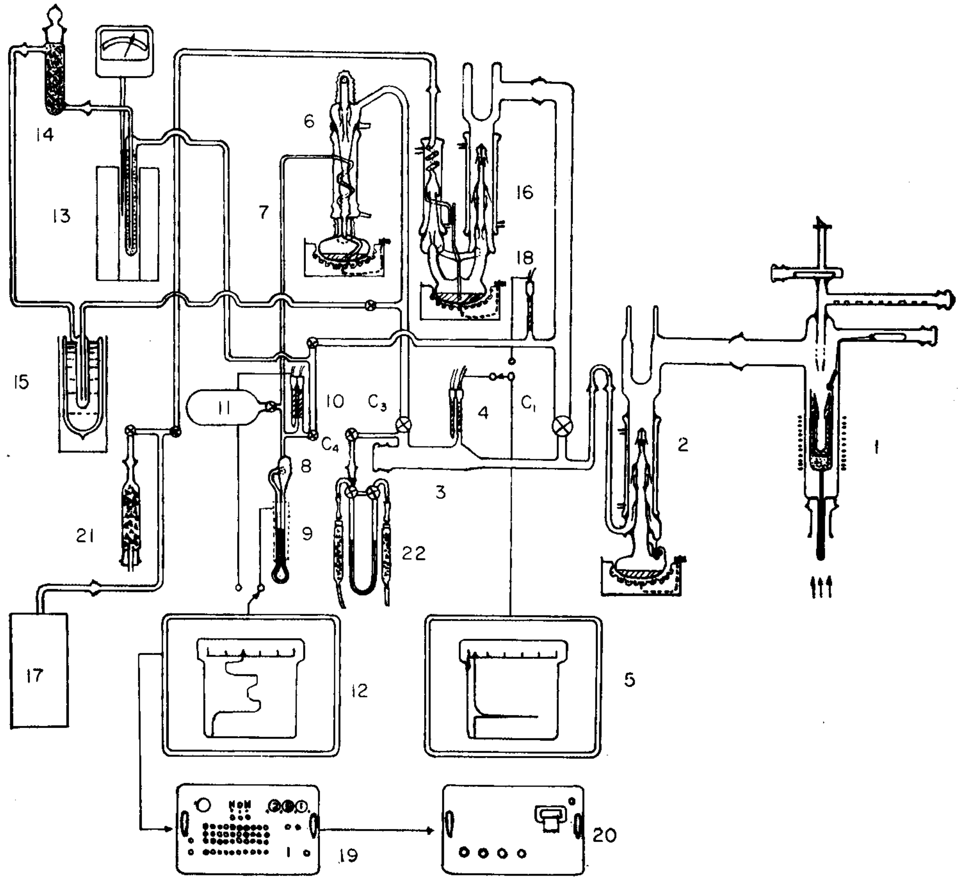


FIG. 1.—Schematic diagram of apparatus

1. Furnace assembly.
2. Extraction pump.
3. Intermediate gas collecting volume.
4. Pirani gauge P.G.2.
5. Automatic self-balancing recorder for gas extraction curve.
6. Collecting pump.
7. Gas collecting volume.
8. Oil manometer.
9. Photocells.
10. Pirani gauge P.G. 3.
11. Expansion volume.
12. Automatic self-balancing recorder for gas analysis.
13. CuO furnace.
14. Absorption tube (P_2O_5) for H_2O.
15. Cold trap for CO_2.
16. Exhaust pump.
17. Mechanical pump.
18. Pirani gauge P.G. 1.
19. Automatic computer for chemical analysis.
20. Digital printer.
21. Silica gel.
22. Silica gel.

C_1, C_3, C_4—stopcocks.

This transfer pump should have a reasonably high critical backing pressure because the pressure in the intermediate collecting volume (3 in Fig. 1) may occasionally build up to 0·1–0·3 mm of mercury. The pump used has, in fact, a speed of 70 litre/sec at 10^{-5}–10^{-2} mm of mercury and a critical backing pressure of 0·7 mm of mercury.

The spherical joint is sealed in place with synthetic rubber packing[10] as shown in Fig. 4, in place of grease, so that any blank caused by grease is reduced.

Gas extraction recording system

Pressure changes in the vacuum furnace chamber measured with an ionisation gauge attached directly to the high pressure side of the extraction pump do not follow accurately a pressure change at the beginning of gas evolution as shown in Fig. 2. Therefore pressure changes were measured indirectly with a Pirani gauge (4 in Fig. 1) attached to the intermediate collecting volume (about 400 ml) between the extraction pump and the collection pump. Pressure changes are recorded with an automatic self-balancing recorder to make gas extraction curves similar to the one illustrated in the right hand portion of Fig. 2. By partly closing the stopcock C_3 (Fig. 1), these curves can be run with greater sensitivity. Valuable information on gas extraction phenomena can be obtained from these recordings.

Stopcock C_3 is used to isolate the furnace system while the gas analysis is carried out. If gas extraction is incomplete, the residual gas evolved from the last sample can be collected during the following blank run in the intermediate collecting volume, and a check made to determine whether the gas extraction is complete or not.

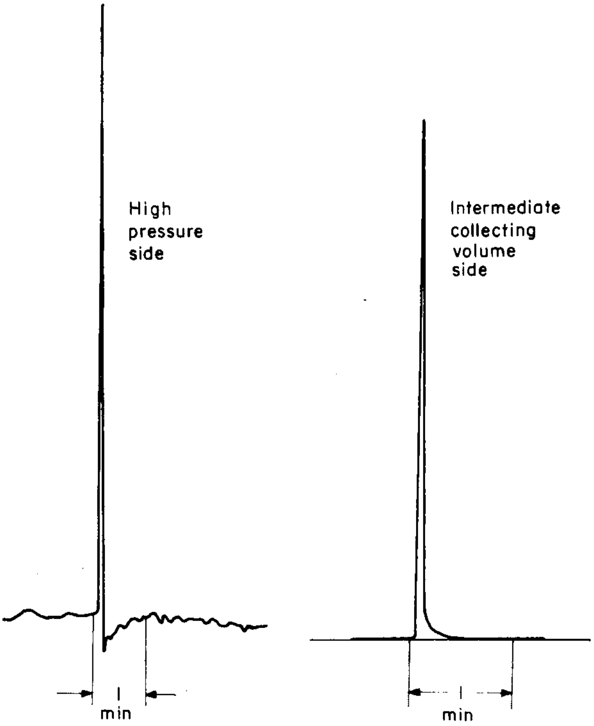


FIG. 2.—Comparison of pressure change between high vacuum side of extraction pump and intermediate collecting volume side.

Collection and circulation pump

The gas extracted is collected into a small collecting volume through the intermediate collecting volume with a newly designed vacuum pump. It is a two-stage mercury ejector pump (6 in Fig. 1),[9] capable of working against a high backing pressure. When the stopcock C_3 is closed, this pump can also be used to circulate the gas in the analysis system. Because the maximum backing pressure of this pump is 9 mm of mercury, the collecting volume can be made small, so that the pressure in it can be so high as to be easily measured.

The effective collecting volume is 75 ml, and the pressure in the collecting volume usually builds up to 3–5 mm of mercury. The speed of the pump is 5 litre/sec at 10^{-3}–1 mm of mercury.

Pressure measurement

Quantitative pressure measurements are made accurately, easily, continuously and rapidly by a newly designed oil manometer, as shown in Fig. 3, because the pressure in the collecting volume is comparatively high.

The oil used is No. 703 or 704 of Dow Corning Silicone. After redistilling and degassing, the oil is poured into the oil pool of the manometer. The manometer is attached to the collecting volume and turned upside down. Once more the oil is degassed by heating the oil pool with a weak flame. For the purpose of avoiding defects, such as absorption and release of gas, the volume of oil used should be a minimum and the contact area between oil and gas should also be a minimum.

An expansion volume of 400 ml (11 in Fig. 1) can be connected by opening a tap if the range of the oil manometer is exceeded by an unexpectedly large evolution of gas.

The volume in which the gases are collected is calibrated by means of a gas burette, and it can be determined with a precision of ±1 %. The temperature of the collecting volume should be held to within ±2° if a high precision measurement is desired. The electric current of the heater of the collection pump and the temperature of the cooling water should be controlled at the same condition as during calibration. The sensitivity (mg/mm of oil) for each gas is calculated, namely, 0·000670 for hydrogen, 0·00532 for oxygen and 0·00931 for nitrogen.

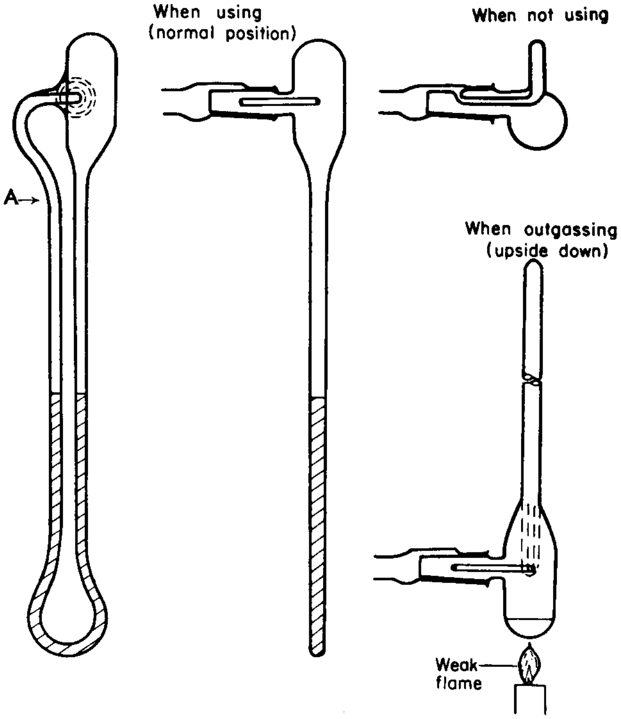


FIG. 3.—Oil manometer.
Below A the tubing is capillary.

The manometer reading is made automatically with photoelectric attachments and recorded on an automatic self-balancing recorder.

Induction heater

An induction heater of 3 kW nominal output at 400 kc/s is used. With the right combination of coil and crucible, a lower power, such as 0·6 kVA (plate voltage × plate current), is dissipated in the graphite to produce a temperature of 2300°. The 16-turn coil is 110 mm high with an internal diameter of 82 mm. The induction heater is provided with a control unit that gives a continuous change of temperature from about 800° to 2300°.

Furnace assembly

The furnace assembly developed by Guldner and Beach[11] has been modified. For the purpose of rapid gas extraction and collection, the dimensions of all parts of the assembly are changed as shown in Fig. 4. This section is an air-cooled Pyrex shell. A joint at the bottom is sealed in place with Dekhotinsky cement and acts as a support for a quartz thimble, which is positioned more uniformly and easily than when suspended by platinum wires from glass hooks. The thimble contains a graphite crucible surrounded by 200–250 mesh graphite powder.

The crucible with a renewable insert is of simple form. The insert, which makes a sliding fit with the crucible, is 75 mm high, 65 mm deep by 26 mm external diameter with a wall thickness of 3 mm, and has a working capacity of 50 g.

A large crucible assembly has the advantages of being able to treat a much greater total weight of metal per run, being more available for a wider range of sample weights, and having a lower rate of increase of bath viscosity, because of the reduction in the ratio of crucible-bath interface area to bath material. The disadvantage of having a somewhat larger blank than for a smaller crucible was a matter for consideration, but in practice the blank is usually as low as 0·01–0·03 ml/30 min at N.T.P.

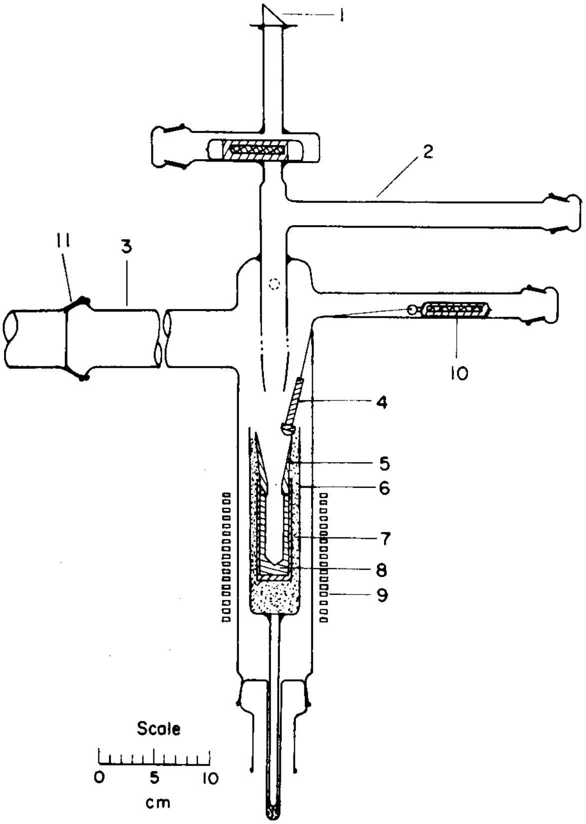


FIG. 4.—Furnace assembly:

1. Prism.
2. Side arm.
3. To diffusion pump.
4. Graphite lid.
5. Graphite funnel.
6. Quartz tube.
7. Graphite powder (200 mesh).
8. Graphite crucible.
9. Induction heater.
10. Magnetic plunger.
11. Rubber packing.

Gas analysis system

Low-pressure methods of gas analysis are rapid and accurate, and they have been used almost exclusively in the present work. Carbon monoxide and hydrogen are oxidised to carbon dioxide and water, respectively, by circulating the gas mixture over heated copper[11] oxide. Water is absorbed with phosphorus pentoxide and carbon dioxide is frozen out in a liquid nitrogen trap. By measuring the pressure drop, each gas is determined. The residual gas is assumed to be nitrogen.

General vacuum system

The system is evacuated by a newly designed all-glass, two-stage mercury diffusion-ejector pump.[9] The speed is 30 to 50 litre/sec at 10^{-5}–10^{-2} mm of mercury, and the critical backing pressure is as high as 5 to 6 mm of mercury. By using this pump it is possible to shorten the outgassing time of the graphite crucible and also to simplify the apparatus on the low pressure side.

Calculation system

Analytical data can be automatically calculated and printed out with a digital electric computer[12] designed newly for chemical analysis. Briefly, if two resistances correspond with the sample weight and the sensitivity of the manometer, respectively, and a third resistance follows the response of the pressure change in the analytical system, and if these are used as three arms in the bridge circuit of the computer, the analytical data can be calculated by automatically matching the resistance of the fourth arm of the bridge circuit.

Safety devices

The most troublesome breakdowns in this apparatus were caused by failure of the cooling water, by breakage of glass parts or by the increase of leaks. The electric power to each part is automatically switched off by safety devices assembled with a pressure gauge or water level meter and meter relay. By these devices, any accident of interruption of the water supply or vacuum break can be avoided. Occasionally at the beginning of heating, a sudden rush of graphite powder used as a heat shield has been experienced. As a symptom of such a sudden rush, the vacuum becomes poorer. At this time a safety device switches off the induction heater automatically and then the sudden rush can be prevented.

Procedure

Sample preparation

A sample weight of 0·1–10 g, but below 10 mm in maximum dimension, is suitable for analysis. Samples are cut by a lathe or shaper without using cutting oil and should be stored in the side arm of the furnace chamber. Twenty or more samples can be placed in the side arm and released in turn by means of magnetic plungers.

Outgassing

Before a new crucible is placed in the apparatus, it is preheated to 400–500° in a stream of argon for about 1 hr. This reduces the time necessary for outgassing and also the crucible blank.

After evacuation of the system, the temperature of the crucible is raised to 2200–2300° and held at this temperature for 1·5–5 hr. The crucible assembly should not be outgassed at a higher temperature, otherwise the rate of evaporation of graphite becomes excessive.

When the outgassing of the graphite crucible is complete, the crucible is allowed to cool to below the extraction temperature. It is then desirable to outgas the bath material little by little because of the reduction of the time necessary for outgassing.

Blanks

The 'blank' gas is collected for 30 min and analysed. The composition normally consists of 30 to 100% of carbon monoxide, 0–70% of hydrogen and is free from nitrogen. The average value of the blank rate at 1850° is equivalent to 0·01–0·03 ml/30 min at N.T.P. This normally is only a small percentage of the gas collected from a sample during a collection time of 1 to 2 min.

The blank is always measured for the 3 min immediately following the collection of gas from a sample. Carbon monoxide and hydrogen blanks do not increase with the number of droppings of the sample but the nitrogen blank tends to increase gradually for some kinds of sample.

Dropping the sample

To obtain a rapid reduction of the oxide, it is generally desirable to introduce the sample into a molten metal bath containing dissolved graphite, except light metal samples. Even if the reaction between bath and sample is violent and a part of the sample or bath material is ejected from the crucible, or if the gas comes off in a rush from the crucible, our experience has shown that lower results are not obtained. It has been observed with the gas extraction curve that ejection of a sample does not happen before gas evolution but at the same time. The crucible lid has been provided but we have not used it, except when outgassing a crucible assembly. By this means, a prolonged stay of gas inside the crucible is avoided. Generally, it seems that high pressure causes incomplete extraction of the gas.

Gas extraction temperature

A gas extraction curve for every kind of sample is determined while the crucible temperature is increased from 800° to 2100°. The selected extraction temperature is 50°–100° higher than the temperature at which gas evolution stops.

Collection time

The observed gas extraction curves show that only 15–60 sec is required for the rate of evolution to become equal to that of the original blank rate. In this apparatus, the gas is usually collected for

1–2 min. If residual gas is found in the intermediate collecting volume during the following blank run, the gas is measured again and analysed.

Gas analysis

The analysis of the gas, the evacuation of the nitrogen and the transfer of the following blank gas into the system, can be completed in 5–7 min. It is undesirable to use anhydrous magnesium perchlorate as an absorber of water vapour in place of phosphorus pentoxide, possibly because of the higher water vapour pressure of the former.

Time required for analysis

The time required for determination of gases in a metal is as follows:

1. Setting furnace assembly, including crucible assembly and sample introduction	30 min
2. Pumping out furnace	5 min
3. Outgassing of crucible at 2200°–2300°	90–300 min
4. Cooling to extraction temperature	5–7 min
5. Blank run	3 min
6. Dropping of sample	0·05–0·2 min
7. Gas collection time	1–2 min
8. Gas analysis (for three elements)	7 min
(for oxygen only)	5 min
9. Calculation by automatic computer	0·1 min
10. Recording with digital printer	0·05 min
11. Evacuation of gas analysis system	0·5–1 min

The total time required for carrying out a complete extraction up to printed results is 7–9 min. If the time required for gas analysis is shortened, the total time may be reduced even more. Analysis of 20 or more samples can be made in 8 hr, including loading, outgassing and gas analysis.

APPLICATION OF GAS EXTRACTION CURVE

Much valuable information about gas extraction phenomena can be obtained from the gas extraction curves measured with a Pirani gauge (4 in Fig. 1).

Gas extraction curve at extraction temperature

From a curve recorded at the extraction temperature, information can be obtained on the following items: state of gas evolution, gas extraction time and gas collection time, successful dropping of sample, state of melting of sample and bath condition.

If dropping, melting and gas extraction are carried out under good conditions, the normal gas extraction curve has a shape similar to curve A in Fig. 5. In such a case, the gas extraction may be completed in as short a time as 15–60 sec.

A gas extraction curve also provides information on whether the results are reasonable or not. For example, when analysing hafnium metal samples, various shapes of gas extraction curve, as shown in Fig. 6, were obtained. The normal gas extraction curve shown in Fig. 6 (A) gives accurate results. Low results are obtained for extraction curves of the type shown in Fig. 6 (B).

When pieces of sample or bath material are dropped one by one into a new crucible, the shape of the gas extraction curve changes gradually and approaches the shape of a normal gas extraction curve as shown in Fig. 7. By this means the state of melting of a metal sample can be observed.

When unexpectedly large amounts of gas evolve from a sample, the curve obtained is similar to B in Fig. 5. In such a case, the tap of the expansion volume should be opened as soon as possible. If a sample is occasionally caught on an upper position of the crucible and does not drop directly into the bath, the curve obtained is as shown in Fig. 5 (C) or (D). Sometimes a similar curve is observed when the bath becomes viscous and a dropped sample floats on the bath.

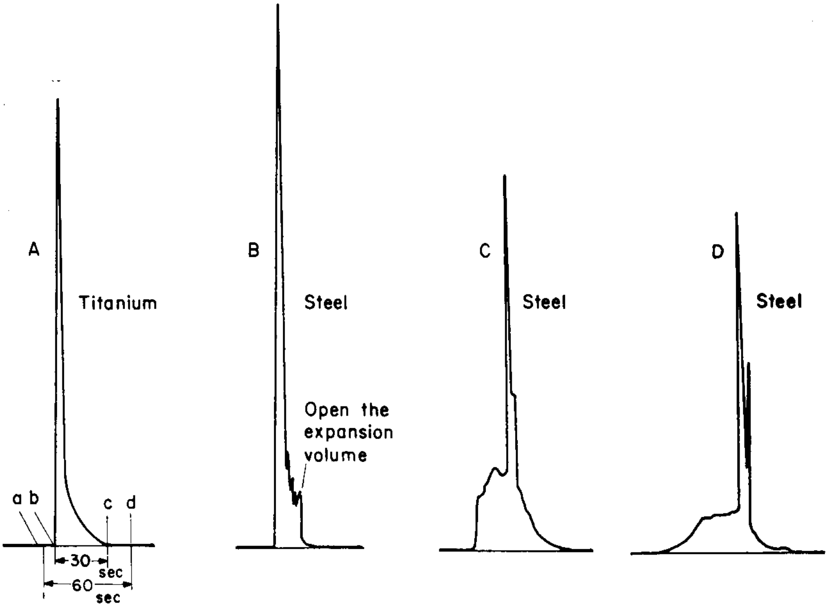


FIG. 5.—Gas extraction curves at extraction temperature:
a–d = collection time,
b–c = extraction time.

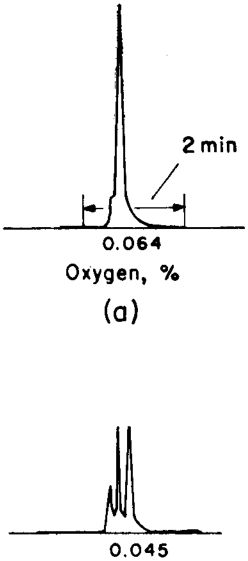


FIG. 6.—Extraction curves of gases in hafnium metal at 1900° (bath material: nickel).

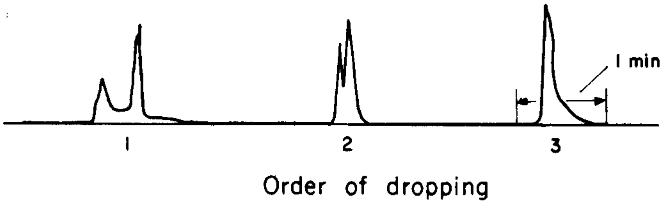


FIG. 7.—Change of gas extraction curve with order of dropping (sample: nickel; temperature: 1850°).

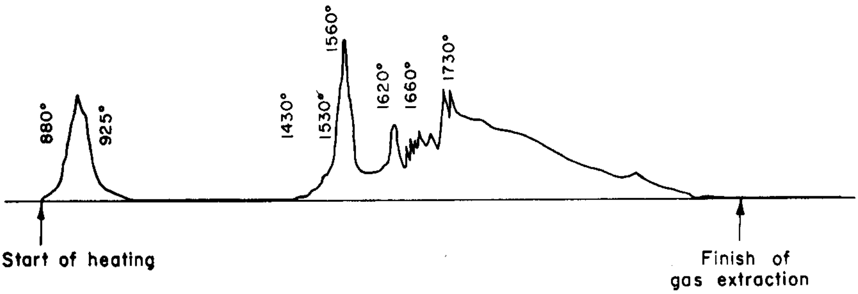


FIG. 8.—Extraction curve of gases in hafnium with increasing temperature.

Gas extraction curve with increasing temperature

From a curve recorded with increasing temperature, information can be obtained on the following items: gas extraction temperature, form of oxides or nitrides, *etc.*

It is very important to decide on a reasonable gas extraction temperature. That is, its temperature should be high enough to complete the extraction but conversely it should be as low as possible in order to avoid the evaporation of sample and bath material. A reasonable temperature can be decided by a gas extraction curve. For example, by this means, the extraction temperature of a sample of hafnium metal in a nickel bath could be decided easily and reasonably. Its extraction curve is shown in Fig. 8.

The total oxygen and nitrogen in a sample can only be obtained by the usual vacuum fusion method. If some information on the form in which the oxygen or nitrogen exists can be obtained, this will be very useful, particularly in the steel industry. By measuring a gas extraction curve with increasing temperature, some information on the form of the oxides or nitrides can be obtained. For example, gas extraction curves of some kinds of steel are shown in Fig. 9. The shape of the curves varies with the kind of sample and it seems that there is a possibility of inference of the form of oxide or nitride.

APPLICATION

Iron and steel

Samples of various kinds and various ranges of oxygen content from 10 ppm up to 650 ppm have been examined. The determinations were made at 1850° without employing a bath material, using sample weights up to 2 g and collecting the gas for 1 min. More reproducible results were obtained than with other types of apparatus and in spite of a very short collection time the analytical results coincided with those found by other investigators, as shown in Table I. The effect of manganese[14] on the determination of oxygen in steel was also studied. As shown in Table II, if a platinum or tin bath is used, the effect of manganese was negligible, but without such a bath more than about 1 % of manganese had a bad effect.

A number of difficulties in the determination of nitrogen by the vacuum fusion method have been reported.[13] Nitrogen results obtained with the old type of apparatus at our laboratory were 20–50 % lower than with the Kjeldahl method. By using the new apparatus the recovery of nitrogen increased, and the nitrogen values were lower by 0–15 % than those obtained by the Kjeldahl method. We think this is caused by the very fast gas extraction. If the same collection time as with oxygen is applied, the extraction of nitrogen is incomplete and the nitrogen content in a blank run gradually increases. Therefore, the amount of nitrogen in the following 26-min blank run was added to the nitrogen value of the last sample. Consequently, the reproducibility was relatively improved as shown in Fig. 10. Yet these results were a little lower than the Kjeldahl values. By using a platinum bath, however, the difference became smaller and in addition, if the collection time was reduced to only 3 min, the recovery of nitrogen was almost complete. Moreover, the effect of manganese on the determination of nitrogen almost disappeared. These results are shown in Table III.

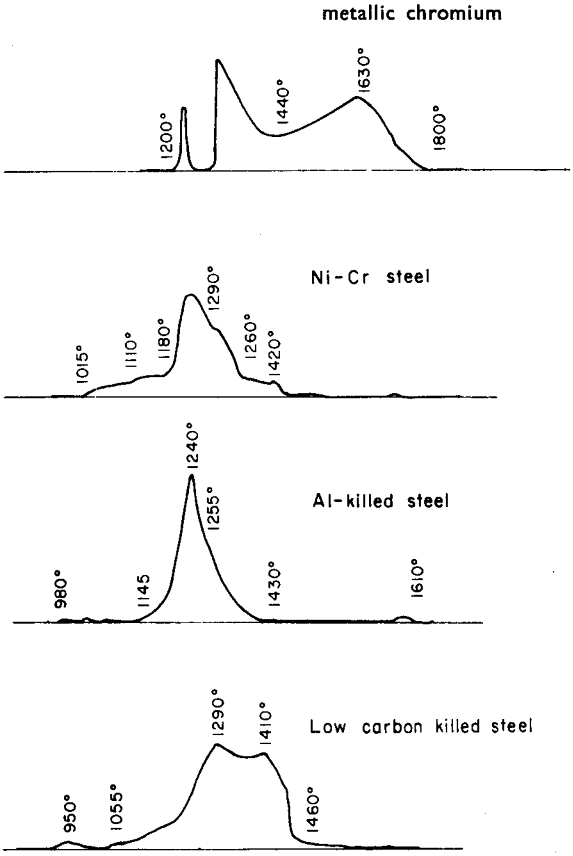


FIG. 9.—Gas extraction curve of various steels and metallic chromium with increasing temperature.

TABLE I.—COMPARISON OF OXYGEN DETERMINATION BETWEEN DIFFERENT LABORATORIES

	Our Laboratory		Gas Analysis[a] Committee		Japan Steel Works Ltd.
	Found, *ppm*[b]	σ,[c] *ppm*	Found, *ppm*[b]	σ,[c] *ppm*	Found, *ppm*
Ni-Cr steel	42	1·3	43	8	—
Low carbon killed steel	54	1·3	58	7	—
Nitriding steel	18	0·8	17	5	—
Carbon steel	79	2·6	—		78
Alloy steel	49	1·8	—		49
Pure iron	176	1·7	—		—
Electrolytic iron	640	10	—		—

[a] Gas Analysis Sub-committee of the 19th Committee in the Japan Society for the Promotion of Science. Collection time: 10–30 min.

[b] Average value.

[c] σ is the standard deviation of the analytical data.

TABLE II.—EFFECT OF MANGANESE ON DETERMINATION OF OXYGEN IN STEEL

Sample	Manganese, %	Oxygen, %		
		None	Pt-Bath	Sn-Bath
Carbon steel	0·35	$0{\cdot}020_3$	$0{\cdot}020_1$	$0{\cdot}019_6$
18-Cr stainless steel	0·50	$0{\cdot}014_0$	$0{\cdot}014_5$	$0{\cdot}018_5$
13-Cr stainless steel	0·65	$0{\cdot}016_8$	—	$0{\cdot}018_8$
Cr-Mo steel	0·79	$0{\cdot}005_3$	$0{\cdot}005_7$	—
Mn steel	1·02	$0{\cdot}002_0$	$0{\cdot}006_2$	$0{\cdot}006_1$
18-Cr-8-Ni stainless steel	1·35	$0{\cdot}003_7$	$0{\cdot}011_0$	$0{\cdot}010_6$

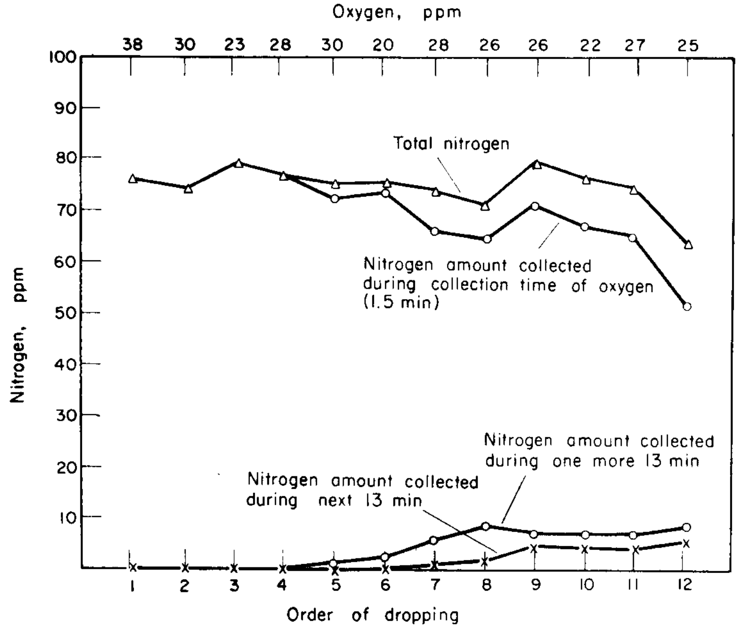


FIG. 10.—Relation between nitrogen recovery and order of dropping (sample: Mn steel; sample weight: 2–2·5 g).

TABLE III.—COMPARISON OF NITROGEN DETERMINATION BY VARIOUS METHODS

Sample	Manganese, %	Nitrogen, %		
		Vacuum fusion method		Kjeldahl method
		None[a]	Pt-Bath[b]	
18-Cr-8-Ni stainless steel	1·35	$0{\cdot}028_0$	$0{\cdot}030_4$	$0{\cdot}029_7$
Mn steel	1·02	$0{\cdot}007_9$	$0{\cdot}009_1$	$0{\cdot}009_6$
Cr-Mo steel	0·79	$0{\cdot}007_2$	$0{\cdot}008_1$	$0{\cdot}008_6$
18-Cr stainless steel	0·50	$0{\cdot}033_6$	$0{\cdot}034_3$	$0{\cdot}035_1$
Carbon steel	0·35	$0{\cdot}004_1$	$0{\cdot}004_4$	$0{\cdot}004_6$

[a] Collection time: 30 min.

[b] Collection time: 3 min.

Acknowledgement—The investigators were assisted by helpful discussions with Drs. H. Ishii and A. Ito and the staff of Industrial Analytical Chemistry, Faculty of Engineering, University of Tokyo.

Zusammenfassung—Eine verbesserte Anordnung für die Freisetzung und Sammlung von Gasen sowie für Messung und Berechnung des Druckes zum Gebrauch beim Vakuumschmelzverfahren wird beschrieben. Es ist für Routineanalyse und für Forschungsaufgaben mit vielseitigen Ansprüchen ausgelegt. Die Sammlung des Gases braucht 1–2 Minuten, einschließlich 15–60 Sekunden zur Freisetzung des Gases. Der gesamte Zeitaufwand für eine fertige Analyse beträgt 7–9 Minuten. Der Blindwert ist 0,01–0,03 ml in 30 Minuten bei 1850°. In 8 Stunden können 20 oder mehr Proben analysiert werden, Aufgeben der Probe, Entgasen und Gasanalyse inbegriffin. Ein neu entworfenes Registriersystem zur Gasextraktion wird beschrieben, mit dem man die günstigsten Bedingungen zur Bestimmung von Gasen in den gebräuchlichsten Metallen aufsuchen kann.

Résumé—On décrit un appareil amélioré pour extraire les gaz, les recueillir, effectuer les mesures de pression et les calculus, pour emploi dans la méthode de fusion sous vide. Il est conçu pour les analyses courantes et les recherches de caractère général. Le temps nécessaire pour recueillir les gaz est de 1–2 mm, y compris 15–60 sec. pour l'extraction des gaz. Le temps total nécessité pour une analyse complète est de 7–9 mn. L'essai à blanc est de 0,01–0,03 ml/30 mn à 1850°. On peut effectuer, en 8 h, l'analyse de 20 échantillons, ou davantage, en comprenant la charge, le dégazage et l'analyse des gaz. On décrit un système enregistreur d'extraction de gaz nouvellement conçu, pour étudier les conditions optimales de dosage des gaz dans les métaux d'intérêt courant.

REFERENCES

[1] R. F. Bunshah *et al.*, *Vacuum Metallurgy*. Reinhold Pub. Co., New York, 1958, pp. 407–432.
[2] Society for Analytical Chemistry, *Report of Symposium on the Determination of Gases in Metals*. Iron and Steel Institute, London, 1960.
[3] J. N. Gregory, D. Mapper and J. A. Woodward, *Analyst*, 1953, **78,** 44.
[4] J. N. Gregory and D. Mapper, *ibid.*, 1955, **80,** 225.
[5] R. S. McDonald, J. E. Fagel and E. M. Balls, *Analyt. Chem.*, 1953, **78,** 44.
[6] E. Booth, F. J. Bryant and A. Parker, *Analyst*, 1957, **82,** 50.
[7] S. J. Bennett and L. C. Covington, *Analyt. Chem.*, 1958, **30,** 363.
[8] N. A. Gokcen, *Trans. Amer. Inst. Mining Met. Petrol. Engineers*, 1958, **212,** 93.
[9] H. Ishii and A. Ito, *J. Vacuum Soc. Japan*, 1958, **1,** 55.
[10] I. Ogahara, *Japan Analyst*, 1960, **10,** 413.
[11] W. G. Guldner and A. L. Beach, *Analyt. Chem.*, 1950, **22,** 366.
[12] I. Ogahara, *Japan Analyst*, in press.
[13] M. Ihida, *ibid.*, 1959, **8,** 786.
[14] D. F. Wood and J. A. Oliver, *Analyst*, 1959, **84,** 436.

Talanta, 1964, Vol. 11, pp. 593 to 599. Pergamon Press Ltd. Printed in Northern Ireland

PIONIERE DER ELEKTROANALYSE

F. SZABADVÁRY
Institut für Allgemeine Chemie, Technische Universität, Budapest, Ungarn

(*Eingegangen am* 3 *September* 1963. *Angenommen* 16 *September* 1963)

Zusammenfassung—Es werden die Erfinder und die bedeutendsten Forscher der verschiedenen Zweige der Elektroanalyse, und zwar der Elektrogravimetrie, pH-Messung, potentiometrischern und konduktometrischern Titration, Coulombmetrie, Polarographie, Amperometrie und der verschiedenen üblichsten Elektroden besprochen. Von der Mehrzahl der erwähnten Persönlichkeiten werden auch die wichtigsten biographischen Daten gegeben.

IM Jahr 1800 begann das Zeitalter der Elektrizität, als Volta seine berühmte "Säule" erfand und damit der elektrische Strom "erfunden" war. Noch im selben Jahr hatten damit Carlisle und Nicholson das Wasser zersetzt,[1] und Cruikshanks beobachtete, dass wenn die Elektrizität der Voltaischen Säule durch eine Metallsalzlösung geleitet wird, daraus Metalle am negativen Pol abscheiden.[2] Das waren die Anfänge einer neuen Wissenschaft, der Elektrochemie, die dann besonders durch die Arbeit von Ritter, Davy und Faraday einen raschen Aufschwung nahm.

Merkwürdiger Weise liess aber die analytische Anwendung des elektrischen Stromes noch ziemlich lange auf sich warten, obzwar man annehmen würde, dass nach Cruikshanks Beobachtung die Elektrogravimetrie sich schnell entwickeln hätte müssen. Tatsächlich liest man aber in den folgenden Jahrzehnten höchstens über einzelne qualitative Nachweise mit Hilfe des elektrischen Stroms. Fischer wies 1812 das Arsen elektrolytisch nach,[3] Cozzi und Gaultier de Claubry empfahlen elektrischen Strom zum Nachweis von Metallen bei toxikologischen Analysen[4,5] während Despretz Blei und Kupfer nebeneinander elektrolytisch nachwies, indem das eine an der Anode, das andere an der Kathode abgeschieden wurde.[6]

DIE ELEKTROGRAVIMETRIE

Die Elektrogravimetrie wurde endlich im Jahr 1864 geboren, also mehr als ein halbes Jahrhundert später als die erste elektrische Batterie. Ihr Erfinder war Wolcott Gibbs. Er bestimmte Kupfer and Nickel in Platintiegeln mit Hilfe der Bunsenschen Batterie. Die Tiegelwand selbst diente als Kathode, während die Anode ein in den Tiegel reichender Platindraht war.[7]

Luckow veröffentlichte 1865 eine ähnliche Methode und behauptet darin sie seit 1860 schon benützt zu haben.[8]

Nun folgten rasch nacheinander Vorschriften zur elektrogravimetrischen Bestimmung weiterer Metalle.

Bedeutend war die Tätigkeit Classens, der zuerst die Rolle der Stromstärke untersuchte und Galvanometer in den Stromkreis schaltete. Er elektrolysierte zuerst unter Erwärmen der Lösung, wodurch die Abscheidung beschleunigt wurde. Ebenfalls Classen ist die erste Monographie über Elektrogravimetrie zu verdanken.[9] Lange Zeit diente der Platintiegel als Kathode, Paweck konstruierte die erste Netzelektrode.[10] Die Quecksilberkathode stammt von Gibbs selbst.[11]

Verwandt zur Elektrogravimetrie, weshalb hier zu erwähnen ist die sogenannte coulombmetrische Analyse, wo unmittelbar Faradays Gesetze zur Bestimmung verwertet werden. Diese verhältnismässig junge Methode wurde 1938 von Szebellédy und Somogyi in die Analyse eingeführt.[12]

ELEKTROMETRISCHE pH-MESSUNG UND ELEKTRODEN

Wie bekannt, gab Nernst die erste quantitative Beziehung für die elektromorische Kraft der galvanischen Ketten.[13] Die elektromotorische Kraft steht danach in Verhältnis mit der Konzentration der Elekrolytlösung. Somit war prinzipiell eine Möglichkeit gegeben zur elektrometrischen Konzentrationsbestimmung. Es fehlte aber die geeignete Elektrode um die Wasserstoffionenkonzentration, der nach der Arrheniusschen Dissoziationstheorie eine bevorzugte Rolle zukam, zu bestimmen. Le Blanc machte 1893 die Beobachtung, dass eine mit Wasserstoff von bekanntem Druck gefüllte Platinelektrode sich gegen Säurelösungen ebenso verhält wie eine Metallelektrode gegen eine entsprechende Metallsalzlösung.[14] Mit Hilfe von Konzentrationsketten unter Anwendung von Wasserstoffelektroden bestimmte dann Salessky die Wasserstoffionenkonzentration von solchen Säure- bzw. Basenlösungen in welchen verschiedene Indikatoren eben Übergangsfarbe zeigten.[15] Soerensen mass den pH-Wert seiner Pufferlösungen schon mit Hilfe von Wasserstoff und Kalomelelektroden.[16] (Kalomelelektrode soll aber Kohlrausch zu physikalischen Zwecken schon im vorigen Jahrhundert verwendet haben.) Cremer beobachtete 1906 bei seinen biologischen Versuchen,[17] dass eine Potentialdifferenz zwischen zwei durch Glasmembran getrennten Lösungen von verschiedenen Wasserstoffionenkonzentrationen auftritt, und stellte auch fest, dass dafür die Membran verantwortlich ist. Haber und Klemensiewicz untersuchten dann diese Frage weiter und fanden dass eine mit neutraler Salzlösung gefüllte dünnwandige Glaskugel ihr Potential ebenso in Funktion der Wasserstoffionenkonzentration ändert wie eine Wasserstoffelektrode. Sie konstruierten 1909 dann die erste Glaselektrode.[18] Obzwar Sie ihrer Elektrode in der Ersetzung der Platinwasserstoffelektroden grosse Zukunft voraussagten, liess diese ziemlich lange auf sich warten. Der grosse innere Widerstand der Elektrode verhinderte nämlich ihren Gebrauch bei der üblichen Kompensationsmethode, man konnte sie nur benützen, wenn mit Quadrantenelektrometer gemessen wurde, das jedoch wegen der Umbequemlichkeit nicht sehr beliebt war. Das richtige Zeitalter der Glaselektroden kam erst mit den Röhrevoltmetern in den dreissiger Jahren unseres Jahrhunderts.

Die Chinhydronelektrode entdeckte Biilmann 1920,[19] die Antimonelektrode Uhl und Kestranek 1923.[20]

POTENTIOMETRISCHE TITRATION

Die erste potentiometrische Titration unternahm Behrend 1893.[21] Er titrierte Quecksilber (I)nitrat mit Kaliumchloridlösung in einer Hg-n/10 $HgNO_3$-n/10 $HgNO_3$-Hg Kette: "Setzt man nun zu einer der Lösungen Chlorkalium, so fällt Quecksilberchlorür aus, der osmotische Druck der Quecksilberionen wird auf dieser Seite geringer und man erhält eine Potentialdifferenz in dem Sinne, dass das Quecksilber unter der mit Chlorkalium versetzten Lösung negativ wird gegen das unter der unveränderten Nitratlösung. Bei weiterem Zusatz von Chlorkalium wird die Potentialdifferenz grösser und zwar bei gleichen Zusätzen zuerst langsam dann immer schneller... Den stärksten Einfluss auf die Änderung der Potentialdifferenz übt der

Zusatz von Chlorkalium in dem Augenblick, in welchem der letzte Rest des Merkuronitrats ausgefällt wird... Weiterer Zusatz von Chlorkalium bewirkt alsdann ein verhältnismäasig langsames Steigen der Potentialdifferenz..." schrieb Behrend, woraus zu sehen ist, dass er den Vorgang auch theoretisch gut zu erklären vermochte.

Vier Jahre folgte dann nichts auf diesem Gebiet, bis dann 1897 Böttger zuerst eine Säure-Basetitration potentiometrisch unter Anwendung einer mit Palladium überzogenen Goldelektrode und der Kompensationsmethode unternahm.[22] Die Redoxtitration war die letzte, die potentiometrisch ausgeführt wurde. Crotogino titrierte 1900 Halogene mit Kaliumpermanganat unter Anwendung einer glatten Platinelektrode.[23]

Zur Messung diente im allgemeinen die Kompensationsmethode. Doch wurden bald auch andere Methoden geschaffen. Wenn man z.B. einen Artikel von Salomon aus 1897[24] aufmerksam durchliest, so findet man, dass dort eigentlich schon ganz genau die sogenannte "dead-stop" Methode beschrieben wurde, die allerdings dann 1926 neu entdeckt wurde.[25]

Unter Anwendung einer polarisierten Elektrode titrierten zuerst 1911 Dutoit und Weisse, die Titration auf Nullpotential wurde gleichzeitig von Pinkhof und Treadwell und Weiss entdeckt,[27] die Differenztitration stammt von Cox.[28]

KONDUKTOMETRISCHE TITRATION

Leitfähigheitsmessungen an Flüssigkeiten wurden für physikalische Zwecke seit Mitte des vorigen Jahrhunderts oft unternommen, sie trugen in hohem Mass zur Ausbildung der physikalischen Chemie bei. Die durch die Neutralisation oder Fällung verursachte Leitfähigkeitsverminderung einer Lösung nützten zu analytischen Zwecken jedoch erst im Jahr 1903 Küster und Grüters aus, die die erste konduktometrische Titration ausführten.[29] In ihrer sehr kurzen Mitteilung berichteten sie aber nichts näheres über die angewandte Einrichtung.

Die moderne Hochfrequenztitration beruht ebenfalls auf der Leitfähigkeitsänderrung der Lösung, sie wurde 1946 unabhängig voneinander von englischen und amerikanischen Forschern entdeckt.[30]

POLAROGRAPHIE

Heyrovský beobachtete 1922 dass das gleichmässig tropfende Quecksilber eine sehr geeignete Elektrode zum Studium von Elektrolysevorgängen bietet. An der sich ständig erneuernden Oberfläche besteht eine grosse Überspannung, man kann sie vollständig polarisieren. Er fand ferner, dass man aus den Potentialkurven die depolarisierenden Komponenten der Lösung qualitativ und quantitativ ermitteln kann.[31] Zur praktischen Vereinfachung dieses Prinzips konstruierten dann 1924 Heyrovský und Shikata den ersten Polarographen.[32] Die Weiterentwicklung der Polarographie, die Oscillopolarographie ist ebenfalls Heyrovský zu verdanken,[33] ebenso wie die sogenannte polarometrische (amperometrische) Titration (1927).[34]

BIOGRAPHISCHE DATEN

Behrend, Robert (1856–1926)

Schüler Ostwalds in Leipzig, von 1897 Professor der organischen Chemie an der Technischen Hochschule Hannover.

Biilmann, Einar (1873–1946)

Professor der Chemie an der Universität Koppenhagen.

Böttger, Wilhelm (1871–1949)

Schüler Ostwalds, von 1910 bis 1938 Professor der analytischen Chemie an der Universität Leipzig.

Carlisle, Anthony (1768–1840)

Arzt im Westminster Hospital, London.

Classen, Alexander (1843–1934)

Von 1883 Professor der analytischen Chemie an der Technischen Hochschule, Aachen.

Cozzi, Andrea (+1852)

Professor der Chemie an der Universität Florenz.

Cruikshanks, William (1745–1800)

Arzt, Professor der Anatomie in London und Chemiker der Artillerie.

Davy, Humphry (1778–1829)

Professor an der Royal Institution, einer der berühmtesten Chemiker, Entdecker der Alkalimetalle, des Bogenlichsts usw.

Despretz, César (1792–1863)

Professor der Physik an der Universität Paris.

Dutoit, Paul (1873–1944)

Von 1898 Professor der physikalischen, von 1918 der analytischen Chemie an der Universität Lausanne.

Faraday, Michael (1791–1867)

Laborant, später Mitarbeiter Davys, endlich Direktor der Royal Institution. Machte bedeutende Entdeckungen sowohl in der Physik (Indukton) wie in der Chemie (Gesetze der Elektrolyse, Benzol usw.)

Foulk, Charles William

Geboren 1869, von 1898 bis 1939 Professor der analytischen Chemie an der Ohio State University.

Gaultier de Claubry, Francois (1792–1878)

Professor der Chemie, später der Toxicologie an der École Supérieure de Pharmacie, Paris.

Gibbs, Wolcott (1822–1908)

Arzt, studierte in Europa neben Rose, Liebig und Dumas, dann Professor im

College of the New York City, später Professor der Chemie an der Harward University, U.S.A.

Haber, Fritz (1868–1934)

Professor der Chemie an der Technischen Hochschule Karlsruhe, von 1912 Direktor des Kaiser Wilhelm Institute für Chemie. Berühmt wegen seiner Arbeit hinsichtlich der Ammoniak-Synthese. Nobelpreisträger für Chemie 1916.

Heyrovský, Jaroslav

Geboren 1890, von 1926 Professor der physikalischen Chemie an der Karls Universität, Prag, seit 1950 Leiter des Polarographischen Instituts der Tschechoslowakischen Akademie. Nobelpreisträger für Chemie 1959.

Klemensiewicz, Zygmunt

Geboren 1886, bis 1939 Professor der Physik an der Technischen Hochschule Lemberg.

Kohlrausch, Friedrich (1840–1910)

Professor der Physik der Reihe nach an der Technischen Universität Zürich, an der Universität Würzburg, Strassburg und endlich Berlin.

Küster, Friedrich Wilhelm (1861–1917)

Schüler von Nernst, wurde 1899 Professor der Chemie an der Bergakademie Clausthal, zog sich 1904 zurück und lebte privatisierend weiter.

Le Blanc, Max (1865–1943)

Zuerst Professor der physikalischen Chemie an der Technischen Hochschule Karlsruhe, dann von 1906 bis 1934 an der Universität Leipzig.

Nernst, Walther (1864–1941)

Schüler Ostwalds, von 1894 bis 1904 Professor der physikalischen Chemie an der Universität Göttingen, von 1904 an der Universität Berlin. Von 1922 Direktor der Physikalisch-Technischen Reichsanstalt. Nobelpreisträger für Chemie 1920.

Nicholson, William (1753–1815)

Beamter des Ostindischen Gesellschaft, dann Schuldirektor in London, dann Privatingenieur, endlich Herausgeber einer wissenschaftlichen Zeitschrift.

Paweck, Heinrich (1870–1941)

Von 1907 Professor der Elektrochemie an der Technischen Hochschule, Wien.

Ritter, Johann Wilhelm (1776–1810)

Praktisierender Arzt in Jena und Gotha, von 1810 in München lebend als Mitglied der Bayrischen Akademie der Wissenschaften.

Shikata, Mazuro

1895 geboren, arbeitete 1923 in Prag, wurde 1924 Professor an der Universität Kyoto, nach 1953 Professor an der Universität Nagoya.

Soerensen, Soeren Paul Lauritz (1868–1939)

Direktor des Carlsberg Laboratoriums in Koppenhagen, Einführer der pH-Bezeichnung.

Somogyi, Zoltán

Assistent an der Universität Budapest. Gestorben durch Kriegsereignisse 1945.

Szebellédy, László (1901–1944)

Von 1938 Professor der anorganischen und analytischen Chemie an der Universität, Budapest.

Treadwell, William Dupré (1885–1959)

Bis 1955 Professor der analytischen Chemie an der Technischen Universität Zürich.

Uhl, Alfred

Geboren 1889, tätig in dem Oesterreichischen Forschungsinstitut für die Landwirtschaft, von 1942 bis 1947 Direktor ebendort.

Volta, Alessandro (1745–1827)

Von 1780 bis 1819 Professor der Physik an der Universität Pavia, Erfinder der ersten elektrischen Batterie (Voltaische Säule, 1800).

Über die im Artikel erwähnten Forscher die im biographischen Teil nicht aufgezählt sind, konnte ich leider überhaupt keine biographischen Daten erfahren.

Summary—The pioneers and the most outstanding research workers in the different branches of electro-analysis—electrodeposition, pH measurement, potentiometric and conductometric titration, coulometry, polarography and amperometry, and the inventors of the commoner types of electrodes are discussed. Brief biographies are given for most of the individuals mentioned.

Résumé—On donne des récapitulations des fondateurs et des chercheurs remarquables dans les différentes branches de l'électroanalyse, la galvanoplastie, la mesure de pH, dosages potentiométrique et conductimétrique, coulométrie, polarographie et ampérométrie, ainsi que des inventeurs des différents types d'électrodes. Brèves biographies sont données pour la plupart des chercheurs.

LITERATUR

[1] A. Carlisle u. W. Nicholson, *Nicholson's J.*, 1800, **4**, 179.
[2] W. Cruikshanks, *ibid.*, 1800, **4**, 187.
[3] N. Fischer, *Schweiggers J.*, 1812, **6**, 27.
[4] F. Gaultier de Claubry, *J. pharm.*, 1850, **17**, 125.
[5] A. Cozzi, *Arch. delle scienze med. fiz.*, 1840, **50**, 208.
[6] C. Despretz, *Compt. rend.*, 1857, **45**, 449.
[7] W. Gibbs, *Z. analyt. Chem.*, 1864, **3**, 334.
[8] C. Luckow, *Dingler's Polytechn. J*, 1865, **177**, 43, 296.
[9] A. Classen, *Quantitative Analyse auf elektrischem Wege.* 1881.
[10] H. Paweck, *Z. Elektrochem.*, 1896, **5**, 221.
[11] W. Gibbs, *Chem. News*, 1880, **42**, 291.
[12] L. Szebellédy u. Z. Somogyi, *Z. analyt. Chem.*, 1938, **112**, 313, 322, 385.
[13] W. Nernst, *Z. phys. Chem.*, 1889, **4**, 129.
[14] M. Le Blanc, *ibid.*, 1893, **12**, 133.

[15] W. Salessky, *Z. Elektrochem.*, 1904, **10**, 204.

[16] S. P. L. Soerensen, *Biochem. Z.*, 1909, **21**, 131, 201.

[17] M. Cremer, *Z. Biol.*, 1906, **29**, 562.

[18] F. Haber ü, Z. Klemensiewicz, *Z. phys. Chem.*, 1909, **67**, 385.

[19] E. Biilmann, *Ann. chim.*, 1921, **15**, 109.

[20] A. Uhl u. W. Kestranek, *Monatsh.*, 1923, **44**, 29.

[21] R. Behrend, *Z. phys. Chem.*, 1893, **11**, 466.

[22] W. Böttger, *ibid.*, 1897, **24**, 253.

[23] F. Crotogine, *Z. anorg. Chem.*, 1900, **24**, 225.

[24] E. Salomon, *Z. physik. Chem.*, 1897, **24**, 55.

[25] C. W. Foulk u. A. T. Bowden, *J. Amer. Chem. Soc.*, 1926, **48**, 2044.

[26] P. Dutoit u. G. Weisse, *J. chim. Phys.*, 1911, **9**, 578.

[27] J. Pinkhof, *Over die Toepassing der Elektrometrische Titration.* Amsterdam, 1919; W. O. Treadwell u. L. Weiss, *Helv. Chim. Acta*, 1919, **2**, 680.

[28] D. C. Cox, *J. Amer. Chem. Soc.*, 1925, **47**, 2138.

[29] F. W. Küster u. M. Grüters, *Z. anorg. Chem.*, 1903, **35**, 454.

[30] J. Foreman u. D. J. Crisp, *Trans. Farad. Soc.*, 1946, **42**A, 186; F. W. Jensen u. A. L. Parrack, *Ind. Eng. Chem., Analyt.*, 1946, **18**, 595.

[31] J. Heyrovský, *Chem. Listy*, 1922, **16**, 256; *Phil. Mag.*, 1923, **45**, 303.

[32] J. Heyrovský u. M. Shikata, *Rec. Trav. chim.*, 1925, **44**, 496.

[33] J. Heyrovský, *Chem. Listy*, 1941, **35**, 155.

[34] *Idem.*, *Bull. Soc. chim.*, 1927, **41**, 1224.

Talanta, 1964, Vol. 11, pp. 601 to 606. Pergamon Press Ltd. Printed in Northern Ireland

LIQUID-LIQUID EXTRACTION OF TUNGSTEN^{VI} WITH TRIBUTYL PHOSPHATE

ANIL K. DE and M. SYEDUR RAHAMAN
Department of Chemistry, Jadapur University, Calcutta, 32, India

(*Received* 12 *September* 1963. *Accepted* 12 *November* 1963)

Summary—A new method has been developed for the rapid extraction of tungsten^{VI} with tributyl phosphate (TBP). Quantitative extraction occurs from 8–10*M* hydrochloric acid using 100% TBP. Tungsten is finally determined spectrophotometrically as thiocyanate. The extractable species is probably $WO_2Cl_2.2TBP$. There are very few interferences. The method is shown to be applicable to an alloy steel.

IN this laboratory tributyl phosphate (TBP) has been used for the extraction of iron^{III} and vanadium^{V}.[1] The extraction studies with TBP have now been extended to tungsten^{VI}. The latter can be extracted from hydrochloric acid solution with TBP. It can then be stripped with water and treated with tin^{II} chloride plus thiocyanate to give a coloured product for spectrophotometric determination. This forms the basis of the method outlined in this paper for extraction and determination of tungsten^{VI} at the milligram level. The method has been successfully applied to an alloy steel.

The thiocyanate method for extraction of tungsten after reduction with tin^{II} chloride or any other suitable reducing agent is well known.[2] Dithiol[3] has been reported to be a good extractant for tungsten. Thenoyltrifluoroacetone[4] in n-butyl alcohol-acetophenone mixture in a strong hydrochloric acid medium has also been used to extract tungsten^{VI}. Other extractants for tungsten are α-benzoinoxime[5] and cupferron.[6]

Pfeifer[12] has previously reported the extraction of tungsten as thiocyanate complex by TBP from 3–6*M* hydrochloric acid. However, his method involves a time-consuming procedure of wet ashing after extraction for subsequent determination of tungsten by the hydroquinone method. The present technique is simple and more rapid.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were carried out with a Unicam SP600 spectrophotometer using matched 1-cm glass cells.

Reagents

Tributyl phosphate: The reagent (Matheson, Coleman and Bell, Cincinnati, Ohio, U.S.A.), b.p. 143–145° at 5 mm, was employed as extractant after purification according to the method of Peppard *et al.*,[13] *viz.*, washing first with 8*M* hydrochloric acid, then with 5% sodium carbonate and finally with water.

Stock solution of sodium tungstate: Prepared by dissolving about 9 g of sodium tungstate (Riedel De Haenag Seelze-Hanover, Germany) in 1 litre of water containing 4g of sodium hydroxide and 8 g of tartaric acid. The solution, standardised by the oxinate method, contained 4·42 mg of tungsten^{VI}/ml. Test solutions for extraction purposes were prepared by dilution of the stock solution so as to contain 188 μg of tungsten^{VI}/ml.

50% *Potassium thiocyanate solution*: Prepared from E. Merck reagent.

7% *Tin^{II} chloride solution:* Prepared from E. Merck reagent in 10*M* hydrochloric acid.

General procedure

A 2-ml aliquot of sodium tungstate solution containing 188 μg of tungsten^{VI}/ml was mixed in a 250-ml separatory funnel with the requisite volume of hydrochloric acid to give an acid concentration of 9*M*. In the experiments involving salting-out agents and diverse ions, the appropriate salting-out agents and foreign ions were added before the acid. The resultant aqueous solution was extracted with an equal volume of 100% TBP for 10 min. Where the effect of TBP concentration was studied, benzene was the diluent. At the end of the extraction, the two layers were allowed to separate. The aqueous phase was retained for measurement of acidity and also for determination of any residual tungsten. Tungsten was then stripped from the TBP layer by consecutive shaking for 10 min with 10 and 5 ml, respectively, of water. To remove any TBP dissolved in the aqueous layer, the back-extract was washed with 5 ml of benzene in a separatory funnel and transferred to a 25-ml volumetric flask. To this 1·5 ml of 50% potassium thiocyanate were added, mixed well and diluted to the mark with 7% tin^{II} chloride in 10*M* hydrochloric acid. The absorbance of the yellow coloured solution was measured at 420 mμ against water within 4 hr.

The optimum period of extraction is 10 min.

RESULTS AND DISCUSSION

Effect of acidity

The solvent extraction behaviour of tungsten^{VI} with respect to TBP was investigated at varying concentrations of hydrochloric acid from 2 to 11*M*. In moderately concentrated acid ($< 6M$), the precipitation of tungstic acid was prevented by the presence of tartaric acid. The distribution ratio (D) was computed from the ratio of the concentrations in the organic and aqueous phases (Table I, Fig. 1). The tungsten in the organic phase was determined as above and in the aqueous phase by the thiocyanate method.[2]

Table I shows that extraction with 100 % TBP (3·66*M*) starts from 2*M* hydrochloric acid and becomes quantitative (> 99%) from 7*M* acid onwards, the aqueous phase after extraction being practically free from tungsten. In Fig. 1, a steep rise in

TABLE I.—DISTRIBUTION RATIO AS A FUNCTION OF ACID CONCENTRATION

TBP concentration, %	HCl, *M* (initial)	Distribution ratio, D^b
100 (3·66*M*)	2	0·08
	3	0·42
	4	1·25
	5	2·9
	6	11·5
	7	61·6
	8·5–10[a]	—
75 (2·74*M*)	4	1·2
	6	6·36
	7	21·4
	9	230
50 (1·83*M*)	4	0·56
	6	3·13
	7	4·7
	9	50·1
25 (0·91*M*)	4	0·21
	6	1·32
	7	3·64
	9	10

[a] Aqueous phase does not contain any detectable tungsten.

[b] $D = \dfrac{[W^{VI}]_{\text{org.phase}}}{[W^{VI}]_{\text{aq.phase}}}$.

the extraction is observed at lower acidities. This is followed by a further rise at higher acidities. The effect is probably caused by salting-out from the aqueous phase by the chloride ion. For quantitative extraction the optimum acid concentration is 8–10*M* hydrochloric acid (equilibrium acidity 6–7*M*). More concentrated acid is not recommended because of trouble in manipulation, although the extraction is quantitative.

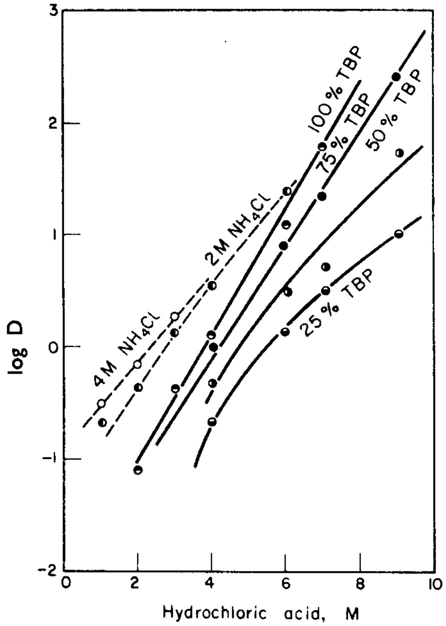


FIG. 1.—Extraction of tungsten^{VI} with TBP as a function of hydrochloric acid concentration in the aqueous phase.

TBP concentration

The concentration of TBP was varied from 25% (0·914*M*) to 100% (3·66*M*) with benzene as diluent. The effect on the extraction was noted at different acid concentrations (Table I). Dilution of the TBP lowers the extraction (Fig. 1). An attempt was made to determine the composition of the extractable tungsten-TBP species by means of a log D *vs.* log C_{TBP} plot.[7] For the plot at 9*M* hydrochloric acid (to obtain four points in all) an extra measurement was taken at a lower concentration of TBP, *i.e.*, 10% TBP (D = 1·3). Below a TBP concentration of 10% the extraction is very poor and the accuracy of measurement unsatisfactory; no further experiments were therefore attempted. The best lines through the points at 6 and 9*M* hydrochloric acid (Fig. 2) give slopes of 1·77 and 2·33, respectively, showing that the extractable species is most probably $WO_2Cl_2{\cdot}2TBP$. This is analogous to other solvated species, *e.g.*, $H[FeCl_4.(TBP)_2]$,[1] $ZrCl_4.2TBP$,[8] $Th(NO_3)_4.2TBP$[9] and $VOCl_3.2TBP$,[1] at high acidity. The optimum reagent concentration is 100% (3·66*M*).

A study of the extraction with 100% TBP from 9*M* hydrochloric acid as a function of tungsten concentration shows that the optimum analytical range is from 50 to

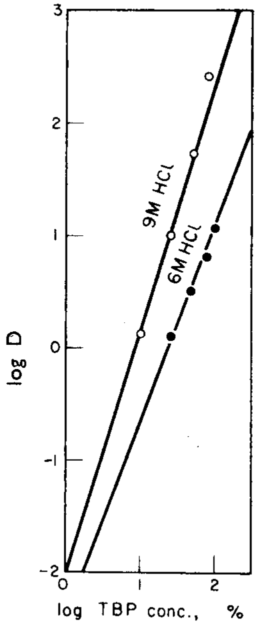


FIG. 2.—Distribution ratio as a function of TBP concentration.

TABLE II.—EFFECT OF AMMONIUM CHLORIDE AND MAGNESIUM CHLORIDE AS SALTING-OUT AGENTS
[376 μg of tungsten^{VI}; 100% TBP]

Salting-out agent	HCl, *M* (initial)	Distribution ratio
2*M* NH_4Cl	1	0·21
	2	0·38
	3	1·34
	4	3·37
	5	5·25
	6	22·5
4*M* NH_4Cl	1	0·32
	2	0·56
	3	1·77
1*M* $MgCl_2.6H_2O$	2	0·46
	3	1·17

470 μg of tungsten. For higher concentrations the relationship between percentage extraction and tungsten concentrations is not linear.

Salting-out agent

The presence of ammonium chloride in the aqueous phase serves to exert a salting-out effect leading to an increased extraction of tungsten^{VI} (Table II). Magnesium chloride in the aqueous phase increases the extraction to the same extent as ammonium chloride. The partition coefficients at lower acidity are found to increase by several orders of magnitude. Under this condition TBP is less combined with acid and so is more available for extraction. This occurs in conjunction with the salting-out function of chloride ion from the added salt. The extractant used was 100% TBP (3·66M).

Diverse ions

Nineteen representative ions were carried through the procedure and examined for interference. The tolerance limit for each, recorded in Table III, represents that concentration of the foreign ion in the presence of which tungsten^{VI} can be extracted and determined spectrophotometrically within ± 2%. It is interesting to note that chromium^{III} and nickel^{II} (10 mg) are not extracted; iron^{III} (10 mg) is co-extracted with tungsten^{VI} but does not interfere in the spectrophotometric determination; zirconium^{IV}, manganese^{II}, phosphate, borate, fluoride, EDTA (10 mg) and citrate, acetate, tartrate (1 g) do not interfere; thorium (1 mg) and uranium^{VI} (0·5 mg) can be tolerated; copper^{II}, molybdenum^{VI}, cobalt^{II}, titanium^{IV} and vanadium^{V} are co-extracted with tungsten and interfere but this can be eliminated by either their preliminary removal or by using suitable masking agents.

TABLE III.—EFFECT OF DIVERSE IONS
[376 μg of tungsten^{VI}; 100% TBP]

Foreign ion	Tolerance limit to ion, μg
Cu^{2+} ($CuSO_4.5H_2O$)	2×10^{3c}
Th^{4+} [$Th(NO_3)_4.4H_2O$]	10^3
Zr^{4+} ($ZrOCl_2$)	10^4
Ti^{4+} [$Ti(SO_4)_2$]	$2{\cdot}7 \times 10^{3a}$
V^{5+} ($VOCl_3$)	4×10^{2b}
Mo^{6+} [$(NH_4)_6Mo_7O_{24}.4H_2O$]	4×10^{2c}
U^{6+} [$UO_2(NO_3)_2.6H_2O$]	5×10^2
Cr^{3+} [$Cr_2(SO_4)_3.18H_2O$]	10^4
Mn^{2+} ($MnSO_4.5H_2O$)	10^4
Ni^{2+} ($NiSO_4.6H_2O$)	10^4
Co^{2+} ($CoSO_4.7H_2O$)	10^{3c}
Fe^{3+} ($FeCl_3.6H_2O$)	10^4
BO_3^{3-} (H_3BO_3)	10^4
PO_4^{3-} [$(NH_4)_2HPO_4$]	10^4
F^- (NaF)	10^4
EDTA (Disodium salt)	10^4
Citrate (Citric acid)	10^6
Acetate (Ammonium acetate)	10^6
Tartrate (Tartaric acid)	10^6

[a] Masked with hydrogen peroxide.
[b] In presence of tartaric acid.
[c] Foreign ion removed first.

Copper^{II} and cobalt^{II} are first removed by extracting with 0·15M TTA in benzene[10,11] at pH 4·5 and 6, respectively. The aqueous phase, after evaporation to small volume, is extracted from 9M hydrochloric acid as usual for tungsten.

Molybdenum^{VI} is extracted with 0·15M TTA in acetophenone from 0·5M hydrochloric acid.[4] Tungsten^{VI} remains in the aqueous phase which is then extracted with TBP.

It has already been shown[1] that tartaric acid reduces vanadium^{V} to vanadium^{IV}

and prevents its extraction with TBP. In order to remove the interference from vanadium^{V} 1 g of tartaric acid was used in the aqueous phase (vanadium$^{(V)}$ = 0·4 mg) during the extraction. Titanium^{IV} in 9*M* hydrochloric acid was masked with hydrogen peroxide (5 ml) and tungsten extracted with TBP.

APPLICATION TO AN ALLOY STEEL

A known weight (0·1 g) of alloy steel (No. 64a, Bureau of Analysed Samples, Ltd., Newham Hall, Yorks., U.K.) was dissolved in 9 ml of concentrated sulphuric acid and 50 ml of water. After the initial reaction was over, the solution was heated, oxidised carefully with 5 ml of nitric acid and evaporated to fumes. Finally, it was diluted with 80 ml of water, boiled to dissolve the salts, filtered to remove silica and washed with 1% sulphuric acid. The filtrate was evaporated to about 25 ml, then diluted to 100 ml in a 100-ml volumetric flask with water. A 4-ml aliquot of this solution was taken in a 250-ml separatory funnel, 0·5 g of tartaric acid added to remove interference from vanadium, followed by 10 ml of 9*M* hydrochloric acid. The solution was extracted twice with 12-ml portions of 100% TBP. Molybdenum^{VI}, tungsten^{VI} and iron^{III} were extracted. From the combined extracts, iron, molybdenum and tungsten were stripped with three 10-ml portions of water. The aqueous phase was evaporated to a small volume (about 2 ml) and transferred to a separatory funnel together with 10 ml of 0·5*M* hydrochloric acid plus 10 ml of 0·15*M* TTA in acetophenone[4] and extracted for 10 min. Molybdenum and some iron were extracted. The aqueous phase containing tungsten^{VI} and iron^{III} was transferred to a 25-ml volumetric flask and tungsten was determined as outlined before.

The results from triplicate analysis of this alloy steel were 5·55, 5·60 and 5·54% of tungsten (reported present: 5·66% of tungsten, 4·11% of molybdenum).

Zusammenfassung—Eine neue Methode zur schnellen Extraktion von Wolfram^{VI} mit Tributylphosphat (TBP) wurde entwickelt. Aus 8–10m Salzsäure ist die Extraktion mit 100% TBP quantitativ. Wolfram wird zuletzt als Rhodanid spektralphotometrisch bestimmt. Die extrahierte Spezies ist höchstwahrscheinlich $WO_2Cl_2.2TBP$. Es gibt nur wenige Störungen. Die Methode läßt sich auf legierte Stähle anwenden.

Résumé—Description d'une méthode d'extraction rapide du tungstène VI par le tributylphosphate-TBP. L'extraction quantitative est effectuée par l'acide chlorhydrique 8 à 10M, en utilisant 100% de TBP. Le tungstène est finalement dosé spectrophotométriquement sous forme de thiocyanate. Le produit extractible est probablement formé en grande partie de $WO_2Cl_2.2TBP$. Il y a très peu d'interférences. Application de la méthode aux alliages d'acier.

REFERENCES

[1] A. K. De and S. K. Majumdar, *Talanta*, 1960, **7**, 1; *Analyt. Chem.*, 1961, **33**, 297.
[2] E. B. Sandell, *Colorimetric determination of traces of metals.* Interscience, N.Y., 3rd Ed., 1957, p. 888.
[3] C. C. Miller, *Analyst*, 1944, **49**, 109; M. B. Hamilton, *Analyt. Chim. Acta*, 1952, **7**, 483; B. Bagshawe and R. J. Truman, *Analyst*, 1947, **52**, 189.
[4] A. K. De and M. S. Rahaman, *Analyt. Chem.*, submitted for publication.
[5] P. G. Jeffrey, *Analyst*, 1956, **81**, 104.
[6] S. H. Allen and M. B. Hamilton, *Analyt. Chim. Acta*, 1952, **17**, 483.
[7] H. Irving, F. J. Rossotti and R. J. P. Williams, *J. Chem. Soc.*, 1955, 1906.
[8] K. Alcock, F. C. Bedford, W. H. Hardwick and H. A. C. McKay, *J. Inorg. Nuclear Chem.*, 1957, **4**, 100.
[9] E. Hesford, H. A. C. McKay and D. Scargill, *ibid.*, 1957, **4**, 321.
[10] A. K. De and S. M. Khopkar, *Z. analyt. Chem.*, 1959, **171**, 241.
[11] A. K. De and S. K. Majumdar, *Analyt. Chim. Acta*, 1962, **27**, 153.
[12] V. Pfeifer, *Mikrochim. Acta*, 1960, 518.
[13] D. F. Peppard *et al.* cited in reference 1, *J. Inorg. Nuclear Chem.*, 1957, **4**, 326.

Talanta, 1964, Vol. 11, pp. 607 to 616. Pergamon Press Ltd. Printed in Northern Ireland

INDIRECT DETERMINATION OF TRACES OF URANIUM USING 1-(2-PYRIDYLAZO-)2-NAPHTHOL

M. R. HAYES and J. S. WRIGHT
United Kingdom Atomic Energy Authority, Springfields Works
Salwick, Preston, Lancashire, England

(*Received* 28 *August* 1963. *Accepted* 2 *October* 1963)

Summary—In the determination of traces of uranium using 1-(2-pyridylazo)-2-naphthol (PAN), solvent extraction of the complex is replaced by the separation of the insoluble complex from homogeneous solution. This is followed by hydrolysis to give free PAN equivalent to the uranium present. An increase in sensitivity of almost 50% results, and the conditions for complex formation require less stringent control. A general method for the determination of uranium in impure liquors is described. Reversed-phase partition chromatography is used for the initial separation of uranium, followed by the use of complexing agents to prevent interference from any residual ions. The method is simple and rapid, and the precision compares favourably with other methods using PAN.

INTRODUCTION

THE use of 1-(2-pyridylazo)-2-naphthol (PAN) as a reagent for the determination of traces of uranium has been described by Cheng,[1] and this work has been extended by Shibata.[2] Cheng reports that the complex with uranium, formed under conditions of controlled pH in the presence of EDTA and cyanide ion to complex other cations, can be selectively extracted into *o*- or *m*-dichlorobenzene or bromobenzene and the absorption measured at 570 mμ. He gives the molar absorptivity as 23,000. Shibata's extension of the procedure permits the use of other solvents, such as chloroform and carbon tetrachloride, which Cheng had found unsuitable under the conditions of his work.

In attempting to adapt the procedure to the analysis of impure uranyl liquors some difficulty was experienced in achieving consistent behaviour. The reagent is largely precipitated in the aqueous medium prescribed, and it was considered possible that the heterogeneous reaction of uranyl ion and solid reagent in suspension could be a factor contributing to the difficulty.

The reagent PAN is readily soluble in a mixture of equal volumes of water and acetone and at approximately pH 9 the presence of a few μg of uranium results in the formation of an insoluble red compound. This precipitate can be separated quantitatively by filtration on asbestos fibre and washed free from excess PAN. If precipitation of the uranium complex is reproducible and a suitable solvent is available to dissolve the complex from the filter, an alternative procedure emerges. This avoids heterogeneous reaction conditions and enables the optical density of the solution of the uranium complex to be measured without interference from the excess PAN.

The non-specific nature of PAN as a reagent leads to interference in the determination of uranium by other metal ions. This effect can be overcome by the use of complexing agents, but where gross amounts of impurity are present a separation of the uranium is essential. A combination of a selective separation procedure, such as reversed-phase partition chromatography (RPPC)[3] with the use of complexing agents, can then be employed to obtain complete freedom from interference.

EXPERIMENTAL

Reagents[6]

All reagents are of analytical-grade quality unless otherwise stated.

1-(2-pyridylazo)-2-naphthol: Supplied by L. Light & Co., Ltd., England; 0·1% w/v solution in acetone.

Asbestos fibre: Powminco Grade A long fibre supplied by Hopkins and Williams Ltd., England.

Kel-F powder: Grade Kel-F 300 low density, supplied by the Minnesota Mining & Manufacturing Co., Ltd., England. Grind to powder with Drikold and liquid nitrogen. Retain the fraction B.S.S.44 to B.S.S.120 for use in preparing the column.

Tributyl phosphate (TBP): Purify the commercial product by refluxing with 0·5% w/v aqueous sodium hydroxide solution. Wash with cold 5% w/v aqueous sodium hydroxide solution until free from di- or monobutyl phosphate. To test this, neutralise a portion of the wash liquid to litmus with nitric acid and add a neutral solution of thorium nitrate. The formation of a precipitate indicates that di- and/or monobutyl phosphate is present and washing must be continued.

Ammonium acetate-aqueous ammonia buffer solution: Dissolve 60 g of ammonium acetate in 450 ml of cold water. Add aqueous ammonia solution to raise the pH to 9·5. Adjust the volume to 500 ml with cold water.

EDTA-ammonium tartrate complexing solution: Dissolve 7·5 g of tartaric acid in 200 ml of cold water. Neutralise to pH 9·0 with aqueous ammonia solution. Dissolve 18·75 g of EDTA (disodium salt) in 250 ml of water and mix with the tartrate solution. Adjust the volume to 500 ml with cold water.

Apparatus[6]

Preparation of asbestos fibre filter. The filter tube is shown in Fig. 1. Hold the perforated porcelain button in position and add a small quantity of a thin aqueous slurry of asbestos fibre to the tube. Apply gentle suction and press lightly with the flattened end of a glass rod to form a uniform pad about 3 mm deep. On removing the suction, water should pass through the filter at 1–2 ml/min; filters with faster rates should be rejected. Wash the pad with 10 ml of hydrochloric acid and finally with water until free from acid.

Shortly before use, wash twice with 5-ml portions of water-acetone solution (1 + 1). The pad may be used repeatedly if it is tamped lightly with the flattened end of a glass rod before re-use.

Preparation of the Kel-F column. The column tube is shown in Fig. 2. Fill the tube with water and press a small piece of cotton wool lightly into the junction with the side tube. Make a slurry of 5 g of Kel-F powder with 5 ml of TBP, set aside for 5 min, then add sufficient water to make a loose slurry. Transfer a small portion of this to the column tube and agitate with a glass rod to remove adherent air bubbles. Allow the Kel-F to settle under gravity while passing a constant stream of cold water through the tube. Repeat the addition of Kel-F several times until the tube is filled to within 1 cm of the reservoir. Insert a cotton wool plug to give a depth of about 1 cm. The rate of elution from the column should be 1·5–2 ml/min and visual inspection should reveal no voids.

Shortly before use, condition the column by passing 25 ml of nitric acid solution (7 + 13) through it. When not required further, wash the column with water until free from nitric acid, then close the outlet tube. Half fill the reservoir with cold water and cover with a watch glass to restrict evaporation.

The life of the column is about 15–20 separations before repacking is required.

Spectrophotometer. All absorption spectra and optical densities were measured using a Unicam S.P.600 spectrophotometer.

Dissolution of PAN-uranium complex following separation on an asbestos filter

Precipitates of the PAN-uranium complex, containing 40 μg of uranium, were formed in a water-acetone (1 + 1) medium buffered to approximately pH 9. The precipitates were separated by filtration on asbestos-fibre filters and washed with water-acetone solution (1 + 1) to remove excess PAN. The residues were extracted by washing with a variety of organic solvents. When solvents immiscible in water were used, the filter and precipitate was first washed with methanol. Methanol, distilled methylated spirit and carbon tetrachloride had no apparent effect. Acetone, chloroform, dichlorobenzene and trichlorethylene all dissolved the complex in varying degrees, giving red solutions, but

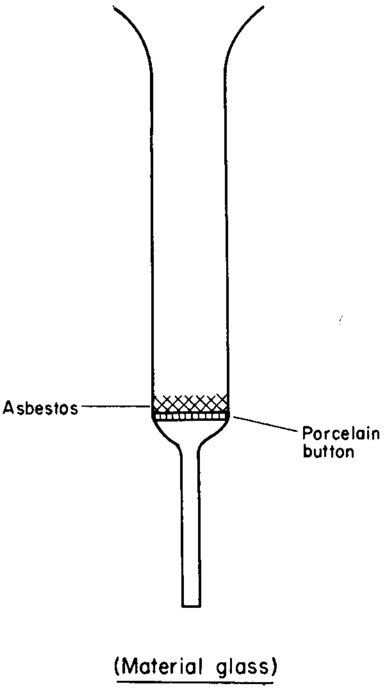


FIG. 1.—Tube for asbestos fibre filter. (Half scale)

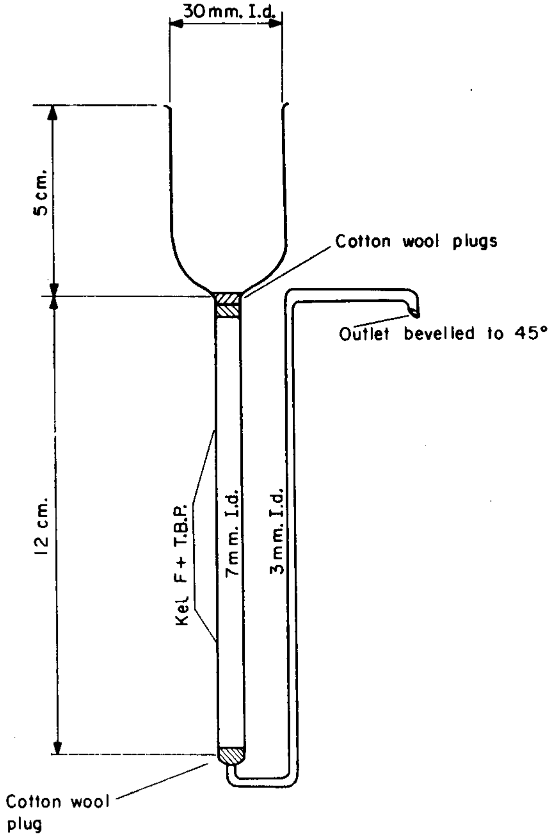


FIG. 2.—Chromatography column tube.

in each case an insoluble pink residue remained on the filter. Tetrahydroxysylvan gave a yellow-brown extract with a dark residual colour on the filter, which on drying showed a pink hue. Similar results were obtained when the complex was formed in a water-methanol medium.

Strong hydrochloric acid dissolved the PAN-uranium precipitates quickly and completely to give a yellow solution. This colour was considered to be that of free PAN resulting from the hydrolysis of the PAN-uranium complex, the optical density of which was found to be proportional to the uranium content of the precipitate. The stability of the PAN colour in hydrochloric acid solution appeared to be adequate and warranted further study of this method for determining the amount of PAN-uranium complex formed.

Absorptiometry

Visible absorption spectra. The visible absorption spectra of solutions of PAN and of PAN-uranium complex in 20% v/v hydrochloric acid solution were identical, both having an absorption maximum at 440 mμ (Fig. 3). Dissolution of the PAN-uranium complex in 20% v/v hydrochloric acid therefore results in complete hydrolysis to the free reagent.

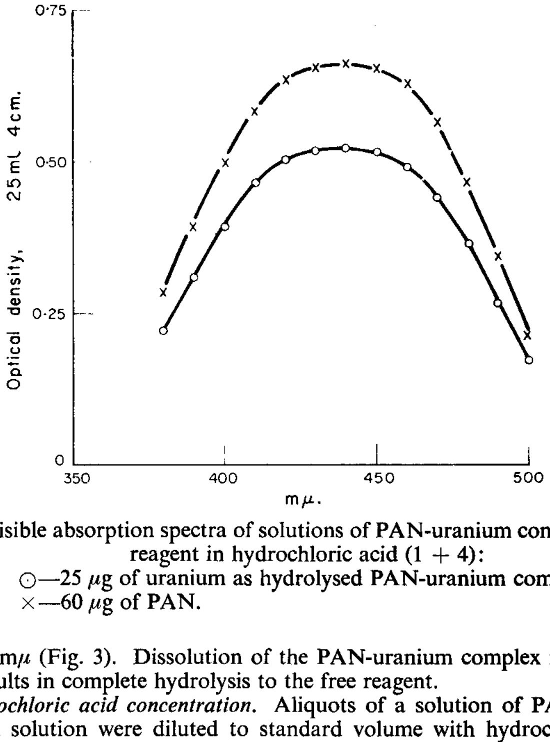


FIG. 3.—Visible absorption spectra of solutions of PAN-uranium complex and of PAN reagent in hydrochloric acid (1 + 4):
○—25 μg of uranium as hydrolysed PAN-uranium complex,
×—60 μg of PAN.

Effect of hydrochloric acid concentration. Aliquots of a solution of PAN-uranium complex in hydrochloric acid solution were diluted to standard volume with hydrochloric acid solutions of differing concentrations and the optical densities measured at 440 mμ. The optical densities were identical within experimental error over a range of concentrations of hydrochloric acid of 5–40%,v/v. At higher concentrations, acid fumes make measurements in the spectrophotometer difficult. In succeeding work, all optical densities were measured in 20% v/v hydrochloric acid solution unless otherwise stated.

Stability of the colour. To test the stability of the solution resulting from dissolution of the PAN-uranium complex in hydrochloric acid, precipitates were formed from varying known quantities of uranium, separated by filtration on asbestos fibre and dissolved in strong hydrochloric acid. The solutions were diluted to standard volume with water, and the optical densities measured at 440 mμ at timed intervals after this dilution. The results are shown in Table I.

The decrease in optical density with time is slow and less than a 1% error results if measurements are made within 1 hr of the dissolution of the precipitate.

Formation of PAN-uranium complex

Solution conditions. PAN-uranium precipitates were formed, using 50 μg of uranium in water-acetone solution (1 + 1) containing ammonium acetate, by adding dilute ammonia solution until a desired pH value was obtained. The precipitates were separated by filtration on asbestos fibre,

TABLE I—STABILITY OF THE COLOUR RESULTING FROM THE HYDROLYSIS OF THE PAN-URANIUM COMPLEX

Time, *hr*	Optical density			
	0 μg U	10 μg U	25 μg U	40 μg U
0	0·013	0·203	0·592	1·005
1	0·013	0·202	0·587	0·990
2·5	0·010	0·196	0·573	0·975
6	0·010	0·196	0·565	0·955
72	0·005	0·155	0·425	0·717

dissolved in hydrochloric acid and the optical densities measured at 440 mμ. The results are shown in Table II.

It is necessary to adjust the solution to at least pH 8 in order to achieve maximum precipitation of the PAN-uranium complex. Over the range pH 8 to pH 10 there is no further effect. Cheng[1] states that in an aqueous medium containing EDTA no significant complex between uranium and the dye is formed below pH 5 and above pH 12. His conditions give maximum complex formation at pH 10 and this is critical, the extent of complex formation falling rapidly above and below this value. The use of an acetone-water medium therefore results in a shift to higher pH for complex formation, but requires much less stringent control. An ammonium acetate-aqueous ammonia buffer adjusted to pH 9·5 was found to give adequate control.

Time required for complex formation. The time taken to complete the reaction between uranium and PAN at room temperature, was measured. The reagents were added to a series of solutions which were then set aside for various time intervals before separation of the complex by filtration. No significant difference in optical density of the final solutions was observed for reaction times in the range 5 to 20 min. The experiment was duplicated at both 40- and 100-μg levels of uranium.

Effect of other ions and limiting of interferences

Cheng and Bray[4] reported that a number of metal ions form coloured chelates and that some of these may be extracted into organic solvents. They also state that EDTA prevents all of the metal ions tested, from reacting with PAN.

A series of experiments was carried out taking 40 μg of uranium, an equal amount of each of 12 other metal ions, and a lower PAN concentration (1 mg), the object of the diminished PAN concentration being to emphasise any interference effects.

These experiments showed that:—

(a) Magnesium and molybdenum are virtually without effect.

(b) Iron, in the bivalent and tervalent states, and nickel form insoluble complexes with PAN and therefore interfere in the determination of uranium.

(c) Copper, lead, chromium, zirconium, thorium, manganese and vanadium capture PAN to the exclusion of uranium, or otherwise affect the precipitation of the PAN-uranium complex forming complexes which are soluble in the buffered acetone-water medium.

Further experiments, using EDTA at the maximum concentration which could be tolerated without affecting the determination of 40 μg of uranium (in the absence of other metal ions), showed that EDTA was not entirely effective in preventing interference from manganese, vanadium, copper, chromium and zirconium. Tartaric acid used together with EDTA eliminated these interferences to a large extent. In conjunction with the full concentration of PAN contemplated (10 mg), up to 190 mg of EDTA or 60 mg of tartaric acid could be tolerated without reducing the recovery of 40 μg of uranium. In admixture the maximum concentrations tolerable were 93 mg of EDTA and 37 mg of tartaric acid. These were reduced to 75 mg and 30 mg, respectively, to allow a margin of safety.

TABLE II

pH	Optical density
6	0·031
7	0·069
8	1·21
9	1·16
10	1·12

Determinations of 40-μg quantities of uranium in the presence of other metal ions using the mixed complexing reagent and 10 mg of PAN are shown in Table III.

A similar experiment was undertaken to show the effect of some anions. The results are shown in Table IV.

TABLE III—EFFECT OF OTHER METAL IONS ON THE DETERMINATION OF 40 μg OF URANIUM

Metal ion	Quantity, μg	Uranium found, μg
Pb	1000	41
Cu	1000	43
Mo	1000	41
Al	1000	42
Fe^{II}	1000	90
	760	45
	500	41
Th	1000	41
V	1000	41
Cr	500	39
Zr	500	34
	300	36
	150	39
Mn	1000	40
Mg	1000	41
Ni	1000	41
Fe^{III}	1000	41

TABLE IV—EFFECT OF SULPHATE, FLUORIDE AND PHOSPHATE ION ON THE DETERMINATION OF 100 μg OF URANIUM

Anion	Quantity, μg	Uranium found, μg
SO_4	10,000	99
	100,000	99
F	100	100
	1,000	98
	10,000	28
PO_4	100	99
	1,000	82
	10,000	NIL

Calibration procedure for the spectrophotometer[6]

Evaporate to dryness aliquots of a standard uranium nitrate solution (1 ml ≡ 40 μg of uranium) covering the range 0–200 μg of uranium. Dissolve each residue in 3 ml of hydrochloric acid solution (1 + 49). Add, with stirring, 2 ml of EDTA-tartrate solution followed by 10 ml of PAN solution and 5 ml of buffer solution in that order. Set aside for 20–25 min at room temperature, then separate the precipitate by filtration on an asbestos fibre filter. Wash the beaker five times with 5-ml portions of water-acetone solution (1 + 1), using each wash to rinse down the tube supporting the filter and allowing each portion to drain through the filter before adding the next. Wash the outside of the filter tube stem to remove crystallised reagent. Finally, wash the beaker and filter with two 5-ml portions of water and allow to drain completely. Dissolve the precipitate from the filter by adding 10 ml of hydrochloric acid (sp. gr. 1·18) in portions, followed by small portions of water, using about 15 ml in all. Collect the eluate in a graduated cylinder containing about 20 ml of water and finally adjust the volume to 50 ml. Measure the optical density of each solution using a 2-cm cell at 440 mμ and correct for the reagent blank value.

Fig. 4 shows a typical calibration curve over a range of 20–175 μg of uranium.

The calibration curve was studied in more detail below 20 μg of uranium, employing standard conditions, but a reduced final volume and increased light path to enhance the sensitivity of the measurements. The results are shown in Fig. 5.

The non-linear behaviour below 18 μg of uranium may result either from a kinetic effect or a solubility effect. The latter is unlikely because the normal calibration curve from 20 μg of uranium upwards passes through the origin.

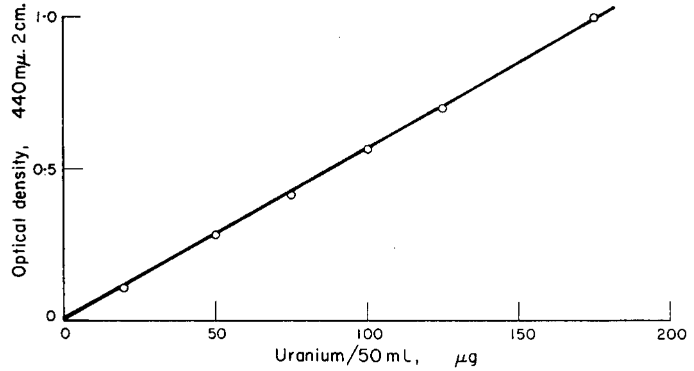


Fig. 4.—Calibration of Unicam SP 600 spectrophotometer for the determination of uranium.

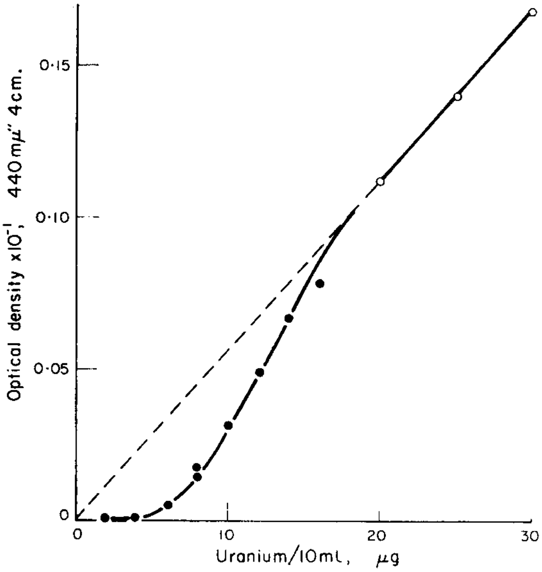


Fig. 5.—Calibration for 0–20 μg of uranium (10-ml volume; 4-cm cell; 440 mμ):
○—○—Calibration between 20 and 175 μg of uranium (see Fig. 4);
●—●—Calibration for 0–16 μg of uranium using stated conditions.

The deviation from linearity confines the lower limit of the method to 20 μg of uranium for normal operation and will cause some error in reagent blank determinations when these fall in the range 4–16 μg of uranium. Because a reagent blank was, however, subtracted from the optical density values used in constructing Fig. 4 and this curve passes through the origin, the effect is apparently not significant. Several more calibrations failed to reveal any effect.

Application of procedure to impure liquors[6]

Procedure. Evaporate a suitable volume of the sample to dryness with a mixture of 1 ml each of nitric and perchloric acids. Dissolve the residue in 5 ml of nitric acid solution (7 + 13) and transfer this solution to a prepared Kel-F tributyl phosphate column. Elute at not more than 2 ml/min. Wash the beaker with four 5-ml portions of nitric acid solution (7 + 13), adding each portion to the column and allowing it to elute at the specified rate before adding the next. Reject the eluate.

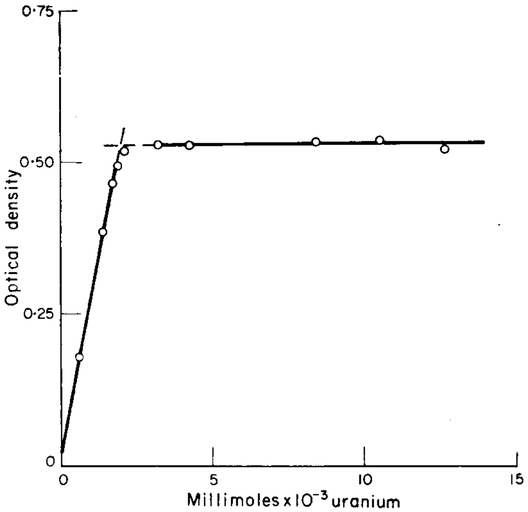


FIG. 6.—Mole ratio of uranium to PAN (separation of uranium using 4·00 × 10^{-3} mmole of PAN).

TABLE V—DETERMINATION OF URANIUM IN IMPURE LIQUORS

Sample no.	Vol. taken, *ml*	Aliquot after RPPC	Uranium found, *μg/ml* (PAN)	Recovery of 50 *μg* of uranium added to sample, %	Uranium by alternative method, *μg/ml*	Alternative method used
1	150	—	0·1	112	0·2	Ether extn./H_2O_2 colour[5]
2	250	—	0·29	108	0·29	Ether extn./H_2O_2 colour[5]
3	25	—	2·6	98	2·5	Ether extn./H_2O_2 colour[5]
4	100	—	0·30	100	0·30	Fluorimetry
5	25	—	3·0	106	2·5	Ether extn./H_2O_2 colour[5]
6	25	$\frac{1}{100}$	840	—	620	Ether extn./H_2O_2 colour[5]
6	2	$\frac{1}{10}$	800	—		
7	25	$\frac{2}{25}$	103	—	85	Ether extn./H_2O_2 colour[5]
8	10	—	12·6	104	10	Ether extn./H_2O_2 colour[5]
8	10	—	12·7	—		
9	25	$\frac{2}{25}$	40	—	36	Ether extn./H_2O_2 colour[5]
10	25	$\frac{3}{50}$	46	110	45	TBP extn./thioglycollate colour
10	2	$\frac{3}{4}$	46	—		

Wash the column with 20 ml of cold water added in two equal portions. Collect the eluate in a 50-ml beaker. Aliquoting may be undertaken at this stage. Evaporate to dryness and continue as described in the procedure for calibration. Carry out a reagent blank determination as above, omitting the sample.

Results on impure sample liquors. The above procedure was applied to a representative selection of samples of impure uranic liquors in which the uranium had been determined by alternative methods. The results are shown in Table V in which the aliquoting of samples after the RPPC separation is indicated

In sample No. 10 a clear yellow band formed at the top of the Kel-F column and was ultimately eluted in the water wash with the uranium. The colour was found to be from cerium^{IV} ion. Because the tolerance of cerium in the PAN determination is not more than 100 μg, 100 mg of sodium nitrite were added to the nitric acid solution of the sample before transferring to the Kel-F column. This served to reduce the cerium to the tervalent state in which it was no longer retained on the column.

Precision test

A number of equal volumes of two samples of impure liquor containing 65–75 μg of uranium were analysed by the procedure given. The results of 19 determinations gave a standard deviation of ±0·96 μg of uranium.

Mole ratio of uranium to PAN in complex and the sensitivity of procedure

The mole ratio of uranium to PAN was determined by making a series of precipitations of the complex from a constant concentration of PAN with varying quantities of uranyl ion. The precipitated complex was then treated as described in the calibration procedure. The results, shown in Fig. 6, indicate a mole ratio of uranium: PAN of 1·0:2·0.

The calibration data shown in Fig. 4 give a molar extinction coefficient of 33,000.

DISCUSSION

In the procedures of Cheng and Shibata the PAN reagent is virtually insoluble in the test solution. This leads to heterogeneous reaction conditions during the formation of the PAN-uranium complex in which the concentration of reagent in solution is very low. Possibly as a result of this, these procedures are extremely sensitive to pH change.

Working in a mixed aqueous/organic solvent, homogeneous reaction conditions apply, and it was found that the PAN-uranium complex forms over a wide pH range, the complex being insoluble. This leads to the possibility of either solvent extraction of the complex or separation followed by dissolution, before colour measurement. Our experience with the PAN-uranium complex has shown that its solution properties in the usual solvents recommended are rather unpredictable. For this reason, separation of the insoluble PAN-uranium complex, followed by hydrolysis to give free PAN equivalent to the uranium, has been used. This gives a molar extinction coefficient of 33,000, an increase in sensitivity of almost 50% over procedures based on solvent extraction of the complex (23,000 and 21,000 by the procedures described by Cheng and Shibata, respectively).

Using the homogeneous reaction conditions a PAN-uranium complex in the molar ratio 2:1 is formed; this is the same as reported by Cheng. The complex is very insoluble, although a possible solubility effect can be detected at concentrations below $4 \times 10^{-6}M$ uranium. This is, however, insufficient to give rise to any significant effect over the normal working range of the method (20–180 μg of uranium). Complexing agents can be tolerated in moderate amounts during the PAN-uranium complex formation but, as with other methods using this reagent, there is some competition for the uranium and a fairly high concentration of reagent must be employed to offset this effect.

In applying the procedure as a general method for the determination of uranium, reversed phase partition chormatography (RPPC) has been used to effect an initial separation of the uranium from other metal ions. An EDTA-tartrate complexing medium is then used to eliminate any possible interference from traces of impurity which pass the initial separation stage. Under the conditions used for the RPPC, thorium, cerium^{IV} and zirconium will be eluted from the column together with the uranium. The amount of these which can be tolerated in the sample solution is therefore limited to that which is effectively complexed, namely, 1000, 100 and 150 μg, respectively. Interference from cerium^{IV} is readily removed by reduction to cerium^{III} with nitrite before RPPC.

Omitting the RPPC stage it was found that 100 mg of sulphate, 1 mg of fluoride and 100 μg of phosphate could be tolerated in the determination of 100 μg of uranium.

The method is applicable to a wide range of impure sample liquors, and is easy and relatively economical to operate. Although the sensitivity is 50% higher than other methods using this reagent, the precision, measured on impure samples, compares very favourably. No evidence of bias has been obtained over the normal working range of the method.

Acknowledgement—The authors thank Dr. J. M. Hill, Managing Director, Production Group, U.K.A.E.A., for permission to publish this paper.

Zusammenfassung—Bei der Bestimmung von Uranspuren mit 1-(2-Pyridylazo)-2-naphthol (PAN) wird die Extraktion des Komplexes durch Abtrennung des unlöslichen Komplexes aus homogener Lösung ersetzt. Die anschließende Hydrolyse liefert eine der anwesenden Uranmenge äquivalente Menge PAN. Die Empfindlichkeit steigt um fast 50% und die Bedingungen für die Komplexbildung erfordern nicht mehr die selbe genaue Kontrolle. Eine allgemein anwendbare Methode zur Bestimmung von Uran in verunreinigten Flüssigkeiten wird beschrieben. Die erste Abtrennung von Uran erfolgt durch Verteilungschromatographie mit umgekehrten Phasen, anschließend werden Komplexbildner zugesetzt, um Störungen durch andere Ionen zu vermeiden. Die Methode ist einfach, geht schnell, und ihre Genauigkeit ist mit anderen Methoden vergleichbar, die PAN verwerden.

Résumé—Dans le dosage des traces d'uranium au moyen du (pyridil-2-azo)-1-naphtol-2 (P.A.N.), le solvant d'extraction du complexe est remplacé par la séparation du complexe insoluble dans la solution homogène. La séparation est suivie d'une hydrolyse redonnant le P.A.N. équivalent à l'uranium présent. Une augmentation dans la sensibilité de presque 50% des résultats et les conditions de formation du complexe nécessitent un controle moins rigoureux. Description d'une méthode générale pour le dosage de l'uranium dans les solutions non pures; une chromatographie de partage par inversion de phase est utilisé pour une première séparation de l'uranium; on traite par un agent complexant pour éviter les interférences dues aux ions résiduels. Cette méthode est simple, rapide et la précision est comparable à celle que l'on obtient avec les autres méthodes utilisant le P.A.N.

REFERENCES

[1] K. L. Cheng, *Analyt. Chem.*, 1958, **30**, 1027.
[2] S. Shibata, *Analyt. Chim. Acta*, 1960 **22**, 479.
[3] T. J. Hayes and A. G. Hamlin, *Analyst*, 1962, **87**, 770.
[4] K. L. Cheng and R. H. Bray, *Analyt. Chem.*, 1955, **27**, 782.
[5] P. G. Report 130(S), The determination of uranium in Springfields effluents and contributory discharges.
[6] P. G. Report No. 436(S), Analytical method for the absorptiometric determination of uranium (pyridyl-azo-naphthol method) following separation by reversed phase chromatography.

Talanta, 1964, Vol. 11, pp. 617 to 620. Pergamon Press Ltd. Printed in Northern Ireland

APPLICATION OF CATIONIC-SENSITIVE GLASS ELECTRODES TO THE STUDY OF ALKALI METAL COMPLEXES—I

THE SODIUM-MALATE SYSTEM

G. A. Rechnitz and J. Brauner*
Department of Chemistry, University of Pennsylvania, Philadelphia 4
Pennsylvania (U.S.A.)

(*Received* 21 *September* 1963. *Accepted* 21 *October* 1963)

Summary—Cationic-sensitive glass electrodes are used to study the weak complex formed by sodium ion and malic acid in aqueous media. The best value of 1·1 ± 0·3 for the calculated formation constant agrees well with literature values. Methods of measurements and calculation are described and evaluated.

INTRODUCTION

Since the recent commercial introduction of cationic-sensitive glass electrodes, a number of useful applications of these electrodes to analytical problems have been reported.[1] Palaty[2] has suggested that such electrodes might also be valuable in the study of complex equilibria, and particularly in the evaluation of formation constants for the alkali metal chelates. Attempts to extend this technique to the study of weak complexes of the alkali metal cations in aqueous solution are reported here.

The sodium-malate system was chosen for consideration because it has recently been studied by neutralisation[3] and nuclear magnetic resonance methods.[4] A value of 2·0 ± 0·3 for the formation constant of the 1:1 sodium-malate complex was reported. Because of certain assumptions concerning the effect of ionic strength and the dissociation of malic acid, however, the absolute value of this constant is probably meaningful only for the specific solution conditions for which the formation of the complex was studied. The principal attractiveness of the cationic-sensitive glass electrode is, in fact, that such restrictive assumptions might be avoided by direct measurements of alkali metal activities.

EXPERIMENTAL

All potentiometric measurements were made using a Beckman Model 76 pH meter on the expanded scale. The Beckman 78137V cationic-sensitive glass electrode and the 39170 fibre-junction calomel reference electrode were employed. In a few cases, a salt bridge containing a portion of the test solution was used, to eliminate the minute leakage of potassium chloride from the reference electrode. During the potentiometric measurements, the temperature was maintained at 30·0° ± 0·1° in the sample vessel by means of a circulating thermostat. Solutions were prepared from reagent-grade chemicals without further purification.

Because the cationic-sensitive glass electrode responds to hydrogen ion, and to ensure complete dissociation of the malic acid, it was desirable to work in alkaline media. Below pH 5, the potential developed by the electrode has been found to be a function of both hydrogen ion concentration and the concentrations of other univalent cations.[1] As a general rule, the hydrogen ion concentration should be 10^3 times less than the concentration of univalent cation under investigation. Tris-(hydroxymethyl)aminomethane was found to be an excellent reagent for pH control. When necessary, ionic strength was controlled with tetramethylammonium chloride.

---

* Present address: Department of Chemistry, St. Peter's College, Jersey City, N.J., U.S.A.

Preconditioning of the glass electrode is essential if reproducible potentials are to be obtained. The electrodes employed here were soaked for a minimum of 48 hr in neutral 0·1*M* sodium chloride solutions. To avoid transfer of interfering species to the sample, the electrode may be rinsed with portions of the test solution before measurement, but wiping or drying of the electrode leads to erratic potentials.

RESULTS AND DISCUSSION

General considerations

A serious limitation to the determination of formation constants by a direct potentiometric measurement arises at once out of the logarithmic relationship between potential and concentration. Because of the nature of this relationship, an error of only 2 mv corresponds to an apparent relative concentration error of about 8·5%. This is particularly serious in the study of weak complexes where the formation of a 1:1 complex with $K = 2$ results only in a 14% decrease in metal ion concentration if the total concentrations of metal ion and ligand are both 0·1*M* initially. Unfortunately, errors of 1 or 2 mv are still to be expected when working with these electrodes. In principle, at least, this problem could be minimised by working with high concentrations of the complexing species, but, apart from solubility considerations, changes in ionic strength and activity coefficient more than nullify any gain in relative measuring accuracy. Table I shows the pronounced effect of ionic strength on the measured potential in sodium chloride solutions.

TABLE I.—EFFECT OF IONIC STRENGTH ON POTENTIAL

Solution	Ionic strength (Adjusted with Mg SO_4)	Potential *vs.* S.C.E., *mv*
0·1*M* NaCl	0·1	152·0
	0·3	149·2
	0·5	147·9
	2·1	146·2
0·01*M* NaCl	0·05	92·3
	0·21	89·2

Methods of attack

All potentiometric methods of determining stability constants are based on the Nernst equation and the mass action laws, but three specific procedures have been employed here:

(1) *Titration method:* A plot of glass electrode potential *vs.* log sodium ion concentration is prepared as a calibration curve in the absence of complexing ligand. A known initial concentration of sodium chloride is then titrated with a standard solution of the ligand, and a plot of potential *vs.* log apparent concentration is prepared. With appropriate correction for dilution effects, the complex formation constant may then be calculated from the original metal ion concentration, the amount of complexing agent added, and the apparent decrease in metal ion concentration at each point along the titration curve. This method of calculating formation constants gives acceptable internal agreement for values calculated at different points along the titration curve, but yields considerable variation in values calculated from separate sets of experiments, probably because of "drifting" of the glass electrode potentials and changes in the slope of the calibration curve which accompany ageing of the electrode.

(2) *Single-point-calibration method:* The apparent formal potential is calculated *via* the Nernst equation from measurements performed on standard solutions of metal ion in the absence of complexing agent. Using this apparent formal potential and the appropriate Nernst slope, the metal ion concentrations in the presence of complexing agent are then calculated directly from the Nernst equation. This method has the advantage over the titration technique of permitting rapid successive measurements on pairs of solutions—one containing a known concentration of metal ion and the other containing metal ion plus ligand in known initial concentrations. The time-dependent effects noted in the titration method can thus be largely eliminated. The necessity of assuming or calculating an appropriate Nernst slope still remains as a significant source of error, however, unless measurements are made on pairs of solutions nearly identical in effective metal ion concentration.

(3) *Emf-difference method:* If it is assumed that in a series of solutions differing only slightly in total metal ion concentration but identical with regard to ligand concentration, pH, *etc.*, the numerical values for the various terms of the Nernst equation remain unchanged, apart from the term in metal ion concentration, then we can write for any such pair of solutions:

$$\mathrm{E}_1 - \mathrm{E}_2 = (\text{slope}) \log \frac{C_{\mathrm{M}_1^+}}{C_{\mathrm{M}_2^+}} \tag{1}$$

Combining equation (1) with the mass action expression for a 1:1 complex, one can derive:

$$\mathrm{E}_1 - \mathrm{E}_2 = (\text{slope}) \log$$

$$\times \frac{C^0_{\mathrm{M^+1}} - \left[C^0_{\mathrm{M^+1}} + C^0_{\mathrm{A^{-n}1}} + \frac{1}{K}\right] - \sqrt{\left[C^0_{\mathrm{M^+1}} + C^0_{\mathrm{A^{-n}1}} + \frac{1}{K}\right]^2 - 4C^0_{\mathrm{M^+1}}\,C^0_{\mathrm{A^{-n}1}}}}{C^0_{\mathrm{M^+2}} - \left[C^0_{\mathrm{M^+2}} + C^0_{\mathrm{A^{-n}2}} + \frac{1}{K}\right] - \sqrt{\left[C^0_{\mathrm{M^+2}} + C^0_{\mathrm{A^{-n}2}} + \frac{1}{K}\right]^2 - 4C^0_{\mathrm{M^+2}}\,C^0_{\mathrm{A^{-n}2}}}} \tag{2}$$

where K is the formation constant of the complex and $C^0_{\mathrm{M^+}}$ and $C^0_{\mathrm{A^{-n}}}$ denote initial concentrations of metal ion and ligand, respectively. Because all initial concentrations are known, equation (2) can be solved for K using the difference of the potentials determined in rapid succession on two similar solutions. This method has the advantage of not requiring a knowledge of the formal potentials involved, and circumvents the difficulties resulting from changes in activity coefficients with drastic alteration in solution composition. The major disadvantage of the method is its relative insensitivity to small changes in K.

A summary of the results obtained using the single-point-calibration and emf-difference methods is given in Table II.

It is immediately apparent that the emf-difference method yields values most nearly corresponding to the formation constants previously reported,[3,4] while the results obtained by the single-point-calibration method are difficult to interpret because of experimental variations. The relatively large variation in calculated values is not surprising, however, when one considers that an emf change of only 0·6 mv will change the calculated formation constant from 0·8 to 1·0 in a typical experiment. That pick-up of carbon dioxide from the atmosphere by the alkaline test solution cannot be of significance here is seen from the similarity of results obtained in runs

TABLE II.—FORMATION CONSTANTS OF SODIUM-MALATE SYSTEM

System	pH	Emf, *mv*	Nernst slope	Formation constant	Method
NaOH+ malic acid	7·0	158·9	55	4·4	(2)
	7·0	154·7	55	4·6	(2)
	6·4	137·6	55	7·0	(2)
				Mean = 5·3	
	8·49	178·0	57	1·0	(3)
	8·50	182·0	57	0·8	(3)
	8·51	176·0	57	1·5	
				Mean = 1·1	(3)
Na_2CO_3+ malic acid	7·7	83·3	55	5·3	(2)
	6·8	80·0	55	6·5	(2)
	8·9	85·6	55	7·7	(2)
	8·3	97·9	55	2·8	(2)
				Mean = 5·5	

using either sodium chloride and sodium carbonate as sources of metal ion. Variations in pH of the test solutions from 7 to 9·8 also produced no significant trends in calculated formation constants. Most of the observed uncertainties must, therefore, be attributed to limitations of the measuring techniques; work is currently in progress to improve these measurements by the use of null-balance potentiometry and will be described in a future report.

Acknowledgement—The authors wish to acknowledge the financial aid of NIH grant GM-10086-02.

Zusammenfassung—Kationenempfindliche Glaselektroden werden zur Untersuchung des schwachen Komplexes aus Na^+ und Äpfelsäure in wäßrigen Medien verwendet. Der Bestwert von 1,1 ± 0,3 für die berechnete Bildungskonstante stimmt gut mit den Literaturwerten überein. Meß- und Berechnungsmethoden werden beschrieben und bewertet.

Résumé—Les électrodes de verre sensibles aux cations sont utilisées pour étudier les complexes peu stables formés par l'ion sodium et l'acide malique en milieu aqueux. La valeur la meilleure de la constante de formation (1,1 ± 0,3) déterminée par le calcul est en bon accord avec les valeurs indiquées dans la littérature. Des méthodes de mesure et de calcul sont décrites et leur précision évaluée.

REFERENCES

[1] G. A. Rechnitz, S. A. Katz and S. B. Zamochnick, *Analyt. Chem.*, 1963, **35**, 1322, and references quoted therein.
[2] V. Palaty, *Canad. J. Chem.*, 1963, **41**, 18.
[3] L. E. Erickson and J. A. Denbo, *J. Phys. Chem.*, 1963, **67**, 707.
[4] L. E. Erickson and R. A. Alberty, *ibid.*, 1962, **66**, 1702.

Talanta, 1964, Vol. 11, pp 621 to 631. Pergamon Press Ltd. Printed in Northern Ireland

INVESTIGATION OF REAGENTS FOR THE COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF CYANIDE—II*

A PROPOSED METHOD FOR TRACE CYANIDE IN WATERS

L. S. BARK and H. G. HIGSON
Department of Chemistry and Applied Chemistry, Royal College of Advanced Technology, Salford 5, Lancashire, England

(*Received* 30 *September* 1963. *Accepted* 7 *November* 1963)

Summary—*p*-Phenylenediamine is used in a König-type reaction for the determination of trace amounts of cyanide in waters. With slight variation in procedure, the method is applicable over the range 0·005–100 ppm.

THE present main methods for the determination of trace amounts of cyanide ion are based on the formation of a dyestuff by the reaction of cyanogen bromide[1] or chloride[2] with an aromatic amine in the presence of pyridine hydrochloride. The fundamental reaction involved is that of the König synthesis[3] of pyridine dyestuffs. A critical consideration of the amines capable of giving dyestuffs suitable for use in the colorimetric determination of cyanide,[4] revealed that only three amines, *p*-aminodiphenylamine, benzidine and *p*-phenylenediamine, formed coloured compounds of any significance. Although benzidine is in use in the United Kingdom standard method (Aldridge method), the range of concentrations that may be determined on the *raw* sample is very limited; furthermore, benzidine itself is a well known and active carcinogen and its use is deprecated by many authorities. It is possible to extend the range of the Aldridge method by suitable modifications,[5] but it is not possible to alter the physiological activity of benzidine.

Of the two other amines, *p*-aminodiphenylamine and *p*-phenylenediamine, the latter compound is more suitable as the dyestuff precursor for the following reasons:

1. It is easily soluble in dilute hydrochloric acid (0·5*M*), whereas *p*-aminodiphenylamine is fairly insoluble. (Prolonged boiling, cooling and filtering is required to produce even a 0·2% solution of *p*-aminodiphenylamine.).
2. When stored in a dark bottle, a 0·2% solution of *p*-phenylenediamine in 0·5*M* hydrochloric acid is stable for at least 6 weeks without noticeable discoloration; *p*-aminodiphenylamine turns blue-purple in less than 1 day.
3. The colour intensity of the pyridine dyestuff with *p*-phenylenediamine is much greater than that with *p*-aminodiphenylamine.[4]
4. With regard to the physiological properties of the two amines, whilst neither has been reported as causing cancer of any type, *p*-phenylenediamine, being a simple mononuclear compound, is more likely to be non-carcinogenic than is *p*-aminodiphenylamine.

---

* Part I: see reference 4.

Factors which may affect the formation of a coloured compound of the pyridine dyestuff type, the intensity of its absorbance and the optimum wavelength to be used in any determination, are:

(i) The treatment of the *raw* sample before colour development;
(ii) The concentration of the reagents used;
(iii) The time allowed for colour development;
(iv) The treatment of the solution after colour development;
(v) The presence of interfering substances in the *raw* sample;

A factor which is of great practical importance is the stability of the reagent.

Treatment of Raw Sample and Colour Development

The initial treatment involves acidification to liberate hydrocyanic acid; this then reacts with added bromine to give cyanogen bromide which is the active species in the König reaction. The acid used in all recommended procedures is glacial acetic acid. A standard volume of glacial acetic acid was used throughout our previous work,[4] and the possible effect of varying the amount of acid used was now investigated.

Reagents

p-Phenylenediamine solution. Dissolve 0·1 g of solid in 50 ml of 0·5*M* hydrochloric acid.

Bromine water. Saturate cyanide-free water with liquid bromine.

Arsenious acid solution. Reflux 2 g of arsenious oxide with 100 ml of cyanide-free water until solution is complete.

Pyridine reagent. Add 3 ml of concentrated hydrochloric acid to a mixture of 18 ml of freshly distilled pyridine and 12 ml of cyanide-free water.

Standard cyanide solutions. Prepared by suitable dilution, with cyanide-free water, of a standardised stock solution.[4]

Procedure

To 4·0 ml of standard cyanide solution, 0·2 ml of bromine water and either 0·1, 0·2 or 0·6 ml of glacial acetic acid were added. The differences in volume were adjusted with cyanide-free water. To each solution 0·2 ml of arsenious acid solution was added; after mixing, the excess bromine vapour in the tube was removed by aeration. To this mixture were added 4 ml of freshly mixed pyridine reagent/*p*-phenylenediamine solution (3·0 ml of pyridine reagent + 1·0 ml of *p*-phenylenediamine solution). The two amines are mixed immediately before use. They must not be added singly because erratic and erroneous results are then obtained.

After thorough mixing the spectra of these solutions were examined using a recording spectrophotometer to establish the best wavelength (isosbestic point) for measurement of the developed colour. This wavelength (515 mμ) was then used to measure the absorbances of the solution compared to water,* with a manually-operated instrument (see Table I).

The effect of varying the amount of acetic acid used is very large. In our previous work regarding the König synthesis[4] the effect of glacial acetic acid was minimised by dilution of the standard cyanogen bromide solutions and the use of an aliquot therefrom, *i.e.*, 0·6 ml of glacial acetic acid was used for acidification of the slightly alkaline cyanide solutions before the formation of cyanogen bromide; then after arsenious acid solution addition, the volumes of the resultant solutions were adjusted to 50 ml. Aliquots of 1·0 or 5·0 ml of these solutions were used, *i.e.*, the equivalent amount of glacial acetic acid used was 0·06 ml in a 5-ml aliquot.

---

* Because we have been particularly concerned with the stability of the aromatic amine reagent employed, we have always preferred to measure absorbances against water of both samples and blanks. With *p*-phenylenediamine the absorbance of a sample may be measured directly against a blank, especially if the amine reagent is reasonably fresh. In the case of a large number of samples, however, the absorbance of the blank may change significantly by the time the final sample is measured against it. Under these conditions measurement of both samples and blank against water is recommended.

TABLE I

Cyanide, *ppm*	Time after mixing, *min*	Absorbance (corrected for blank)		
		Glacial acetic acid, *ml*		
		0·1	0·2	0·6
0·1	15	0·055	0·028	0·004
	40	0·055	0·028	0·004
0·2	15	0·100	0·061	0·011
	40	0·099	0·059	0·014
0·3	15	0·148	0·088	0·013
	40	0·145	0·087	0·016
0·4	15	0·191	0·114	0·015
	40	0·192	0·116	0·018
2·0	15	1·114	0·630	0·043
	40	1·066	0·590	0·040

TABLE II[a]

Cyanide, *ppm*	Time after mixing, *min*	Absorbance (corrected for blank)			
		Acetic acid	Bromine water	Hydrochloric acid	Phosphoric acid
0·1	20	0·034	0·095	0·100	0·052
	25	0·033	0·098	0·101	0·052
	30	0·031	0·098	0·101	0·052
	35	0·029	0·097	0·100	0·050
	40	0·028	0·097	0·099	0·050
0·25	20	0·082	0·246	0·247	0·144
	25	0·077	0·254	0·255	0·142
	30	0·075	0·257	0·255	0·142
	35	0·074	0·255	0·255	0·142
	40	0·071	0·253	0·255	0·142
0·5	20	0·160	0·503	0·503	0·287
	25	0·154	0·511	0·510	0·285
	30	0·150	0·513	0·511	0·284
	35	0·146	0·510	0·509	0·284
	40	0·142	0·509	0·509	0·282
1·0	20	0·319	1·006	1·001	0·575
	25	0·309	1·030	1·020	0·573
	30	0·304	0·065	1·041	0·571
	35	0·300	1·080	1·050	0·569
	40	0·295	1·097	1·057	0·566

[a] All measurements at 515 mμ.

Because the amount of acetic acid used altered the absorbance of the colour developed, it was decided to investigate the effect of other acids. The acids chosen were concentrated hydrochloric acid, phosphoric acid and the acidity from the addition of saturated bromine water alone. The results were compared with those obtained using acetic acid. Because slight variations in absorbances with time were noted in the work with glacial acetic acid, the absorbances were measured at various fixed time intervals under standard conditions.

The procedure followed was as before, except that to the standard cyanide solution (4·0 ml) and bromine water (0·2 ml) one of the following was added:

(a) 0·2 ml of glacial acetic acid,
(b) 0·2 ml of cyanide-free water (acidity from bromine water alone),
(c) 0·2 ml of concentrated hydrochloric acid (sp. gr. 1·18),
(d) 0·2 ml of concentrated phosphoric acid (sp. gr. 1·75).

Calibration curves obtained from these results (Table II) are shown in Fig. 1.

The colour developed in the presence of all of the acids investigated obeys Beer's Law. Hydrochloric acid does not alter the absorbance of the solution from that when acidified only with bromine water, but both acetic acid and phosphoric acid greatly decrease the absorbance at all times.

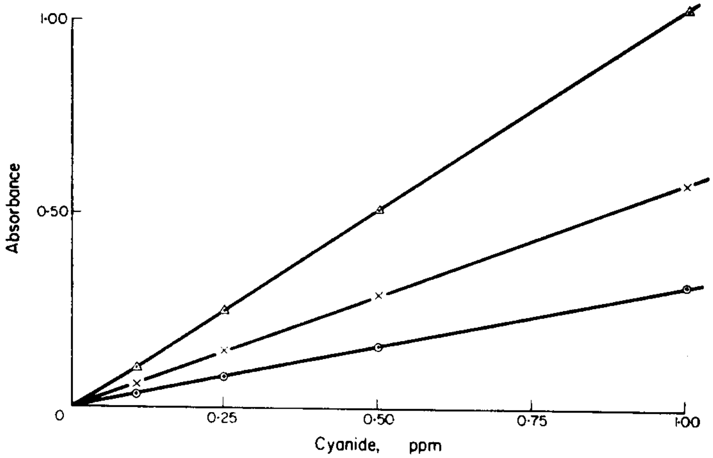


FIG. 1.—Absorbance with various acids (after 25 min; 515 mμ):
—△— water or concentrated hydrochloric acid,
—×— phosphoric acid,
—⊙— glacial acetic acid.

In order to show the effectiveness of *p*-phenylenediamine compared to benzidine, which is at present accepted as the standard reagent for determination of cyanide, the two were compared under conditions employed with the standard reagent (Aldridge procedure), except that the sample solution was acidified with bromine water alone, with bromine water plus concentrated hydrochloric acid or with bromine water plus glacial acetic acid.

The results are presented in Table III; the curves obtained from (a) and (d) are shown in Fig. 2. On the same scale, the curves from (a), (b), (c) and (f) are coincident for much of the range. Thus, neither glacial acetic acid nor hydrochloric acid has any appreciable effect on the absorbances produced when using benzidine. In the presence of acetic acid, the absorbances developed with *p*-phenylenediamine and benzidine are similar. When using conditions where no decrease in absorbance of the *p*-phenylenediamine colour occurs, this reagent gives a much greater absorbance than does the same concentration of benzidine.

Because the type of acid used has a significant effect, the possible effects of varying amounts of reagents were investigated for both *p*-phenylenediamine and benzidine. Increasing the amount of bromine water from 0·2 ml to 2·0 ml had no effect.

Using a 10-ml or a 5-ml *raw* sample and equal amounts of the other reagents had

TABLE III

Cyanide, *ppm*	Absorbance[a] after 30 min (corrected for blank)					
	Benzidine			*p*-Phenylenediamine		
	Bromine water	Hydrochloric acid	Acetic acid	Bromine water	Hydrochloric acid	Acetic acid
0·1	0·011	0·011	0·014	0·018	0·018	0·007
0·2	0·027	0·028	0·030	0·090	0·090	0·020
0·5	0·067	0·065	0·072	0·280	0·281	0·063
1·0	0·131	0·130	0·136	0·561	0·560	0·128
1·5	0·182	0·180	0·185	0·840	0·840	0·190
2·0	0·237	0·240	0·247	1·160	1·162	0·251
	(a)	(b)	(c)	(d)	(e)	(f)

[a] 515 mμ for *p*-phenylenediamine, and at 522 mμ for benzidine;[5] 0·2% solutions of the two amines in 0·5*M* hydrochloric acid were used.

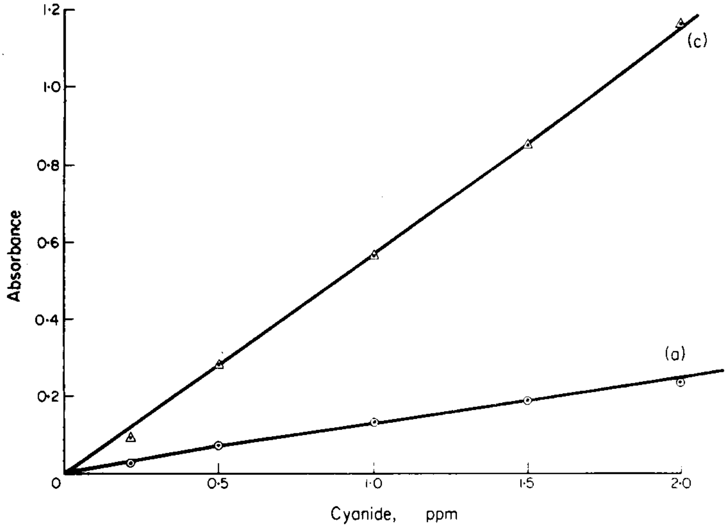


FIG. 2.—Absorbance obtained with 0·2% w/v solutions of:
(a) benzidine (522 mμ),
(c) *p*-phenylenediamine (515 mμ).

no significant effect. Less than a 0·4% difference in the absorbances of the two solutions was noted over a range of concentrations of cyanide.

Treatment of Solution After Colour Development

For samples containing cyanide at concentrations greater than 2·0 ppm, the procedure must be altered because the absorbance becomes so great as to make measurement by normal methods impracticable. In earlier work[5] we have shown that the upper range of the Aldridge method using benzidine could be extended by a modification of the method of Baker *et al.*,[6] using aqueous alcohol to dilute the developed colour. The present method was investigated using a similar dilution technique.

To 2·0-ml samples containing 0·0, 0·5, 1·0, 4·0, 5·0 and 10·0 ppm of cyanide in 25-ml volumetric flasks, 2·0 ml of bromine water and 0·1 ml of concentrated hydrochloric acid were added. After 5 min, 0·4 ml of arsenious acid solution was added and 4·0 ml of freshly mixed pyridine/*p*-phenylenediamine. After 1 min, 5 ml of ethyl alcohol were added and cyanide-free water to make each volume 25 ml. The best wavelength for measurement was ascertained, then the absorbance of the solutions was measured in 1-cm cells, compared to water, at this wavelength, using a manually operated spectrophotometer.

The results are shown in Tables IV(a) and IV(b). The isobestic point for solutions processed by the above dilution technique was at 520 mμ. This shift of wavelength from 515 mμ (isosbestic point for 2·0-, 4·0- or 5·0-ml sample is 515 mμ and for 10·0-ml sample 512 mμ, both using the non-dilution technique) must be caused by a concentration effect.

TABLE IV(a).—ABSORBANCE OF REAGENT BLANK SOLUTION

Time after mixing, *min*	Absorbance compared with water
20	0·018
30	0·017
40	0·018
50	0·020
60	0·020

TABLE IV(b).—ABSORBANCE OF SOLUTIONS CONTAINING CYANIDE

Time after mixing, *min*	Absorbance (Corrected for blank)				
	Cyanide, *ppm*				
	0·5	1·0	4·0	5·0	10·0
20	0·035	0·078	0·366	0·486	1·010
30	0·034	0·077	0·365	0·485	1·005
40	0·033	0·076	0·367	0·487	1·006
50	0·033	0·075	0·363	0·482	0·999
60	0·033	0·074	0·362	0·477	0·995

The dilution procedure is fairly satisfactory when using *p*-phenylenediamine solution as reagent but offers no advantage over dilution of the *raw* sample before the addition of bromine and amine.

For samples containing trace amounts of cyanide and using benzidine as the dye precursor, Nusbaum and Skupeko[7] extended the lower range of the Aldridge method by extracting the pyridine dyestuff into n-butanol. The procedure of Nusbaum and Skupeko was followed, except that *p*-phenylenediamine solution (0·2% w/v) was used in place of benzidine. The developed colour was extracted using 10 ml of n-butanol. The absorption spectrum shows a maximum at 480 mμ. Some typical results are included in Table V.

Small bubbles occasionally form in the butanolic extract in the optical cell. These are water bubbles forming from a slightly supersaturated water/butanol solution; they may be removed by using a 5% solution of disodium phosphate to break any emulsion formed and centrifuging the butanol extract for 2–3 min. The phosphate does not have any appreciable effect on the actual absorbances. However, the extraction procedure involves one or two more steps in the over-all procedure and this is

TABLE V

Cyanide, *ppm*	Absorbances (corrected for blank)	
	Solvent extraction (480 mμ)	Without extraction (515 mμ)
0·01	0·018	0·009
0·02	0·032	0·021
0·05	0·065	0·049
0·10	0·167	0·101
0·20	0·323	0·201
0·30	0·496	0·298
0·50	0·838	0·509

an obvious disadvantage. Although there is a 50% increase in the absorbance, at the lower end of the range the reproducibility using solvent extraction is not as good as without extraction. With a very low concentration of cyanide, more than one extraction is necessary and the resultant volume errors tend to remove the advantage of increased colour absorbance. The method is not recommended.

Thus, the procedure as so far envisaged is:

Using a 4·0-ml *raw* sample, add 0·2-ml of bromine water and 0·1 ml of concentrated hydrochloric acid. Mix well, add 0·2 ml of arsenious acid solution followed by 4·0 ml of freshly mixed pyridine/*p*-phenylenediamine. The absorbance is measured against water in 1-cm cells, at 515 mμ, after 30 min.

The results are as described (Fig. 1). It is possible to use the method down to 0·005 ppm with an accuracy of 1–2%, the main source of error being the measurement of the small volumes of reagents.* However, because industrial samples of cyanide (effluents, *etc.*) are relatively unlimited, these sources of error can be minimised by using a larger sample size. To ensure an adequate excess of bromine in the sample, the amount of this reagent used must, of course, be increased. The following procedure was adopted for samples of "unlimited" size:

Treat 40 ml of the *raw* sample in a 50-ml volumetric flask with 2·0 ml of saturated bromine water and 0·1 ml of concentrated hydrochloric acid, then thoroughly mix. After 5 min, 0·4 ml of arsenious acid solution is added and the total volume adjusted to 50 ml with cyanide-free water. A 5·0-ml aliquot of this mixture is treated with 4·0 ml of freshly mixed pyridine/*p*-phenylenediamine. The solutions are thoroughly mixed and the absorbance of the resulting solution is compared to that of water at 515 mμ, at various times after mixing.

The results obtained showed that the colour obeys Beer's Law. To extend the upper range of the method, dilution of the sample before addition of reagents enables the method to be used from 0·001–100 ppm. Some typical results using this procedure are given in Table VI.

The absorbances after 30 min obtained from 5·0-ml of the treated mixture are shown graphically on Fig. 3.

For small concentrations of cyanide this procedure has no advantage over the original procedure other than that of increasing the accuracy by decreasing the relative volume errors in the sample size. For relatively large concentrations of cyanide (10 ppm or greater), however, the use of a 1·0-ml sample and dilution to 40·0 ml reduces the concentration of other material present by a factor of 10. This may reduce interferences (see later) to a tolerable level in some instances.

---

* For 4-ml samples a 4-ml grade A pipette was used, and for volumes of reagents of less than 1-ml a 1-ml pipette (graduated into 0·01 ml) was used.

TABLE VI

	Cyanide in "raw" sample, *ppm*	Cyanide $\mu g/5$ *ml*	Absorbances (corrected for blank)		
			Time after mixing, *min*		
			20	30	40
a	0·001	0·004	0·002	0·003	0·003
a	0·005	0·02	0·005	0·004	0·004
a	0·025	0·1	0·027	0·026	0·026
a	0·050	0·2	0·048	0·047	0·047
a	0·100	0·4	0·096	0·102	0·104
a	0·250	1·0	0·218	0·248	0·246
b	20·0	2·0	0·425	0·448	0·451
b	40·0	4·0	0·933	0·990	0·995
b	100·0	10·0	2·32	2·55	2·45

a: 40·0-ml *raw* sample.
b: 1·00-ml *raw* sample.

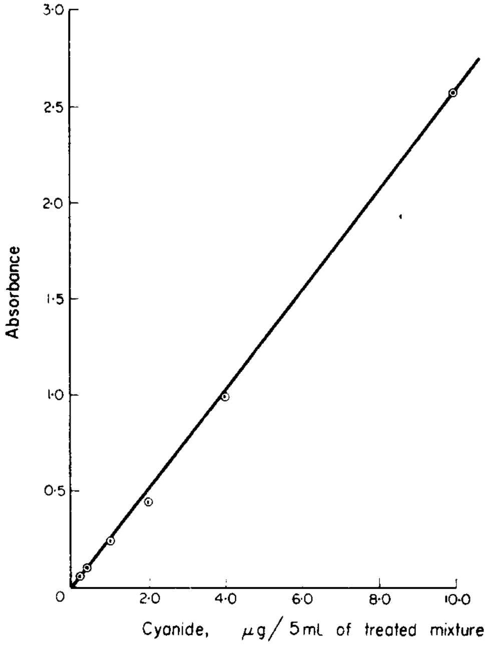


FIG. 3

Interferences

Interfering substances may be divided into:

(i) Those which react with bromine and form cyanogen bromide under the conditions of the reaction; these substances give high values for the cyanide present.

(ii) Those which prevent the cyanide ion from forming cyanogen bromide and hence give low results.

In the first class of substances, the most important is the thiocyanate ion, which reacts with bromine to produce cyanogen bromide. Both methods developed, employing *p*-phenylenediamine, may be used to determine the amount of thiocyanate present. The difference in reaction weights of the cyanide and thiocyanate ions is reflected in the absorbances produced, *viz.*

0·2 ppm of cyanide gives, on reaction, an absorbance of 0·200,

0·2 ppm of thiocyanate gives, on reaction, an absorbance of 0·100.

It is possible to determine the two ions in admixture, using the following procedure based on the non-volatility of thiocyanic acid. The total cyanogen bromide-producing substances in one aliquot of the sample are determined in the proposed manner. A second aliquot of the sample is acidified with either trichloracetic acid or boric acid, heated to 90–100° and aerated by a slow stream of air bubbles for 10–15 min. The evolved hydrocyanic acid is collected in 0·1*M* sodium hydroxide solution and the cyanide content of the resulting solution determined as previously described. The residual thiocyanate in the acidified solution may also be determined (like hydrochloric acid, trichloracetic acid and boric acid have no effect on the absorbance produced by bromine water alone).

Cyanates, hexacyanoferrate (II) and hexacyanoferrate (III) are without effect. Cyano-complexes of zinc and copper, however, yield cyanogen bromide when treated with bromine water, and it is necessary to remove free (uncomplexed) cyanide ion by the aeration procedure described.

Iron^{II}, nickel^{II} and copper^{II}, in quantities of 100 ppm, produce a ten-fold, three-fold and two-fold decrease in the concentration of cyanide found, respectively.

Of the other metal ions probable in effluents, manganese, lead, zinc, mercury^{II} and silver do not interfere in amounts up to at least 100 ppm in the solution as tested.

Reducing and/or oxidising agents present do not interfere except by consuming the bromine water or arsenious oxide solution, respectively.

Free chlorine which is often present in trade effluents, does not interfere; the cyanogen chloride formed has the same effect as cyanogen bromide.

Non-oxidising or non-reducing ions present, such as borate, bromide, carbonate, chloride, nitrate, phosphate and sulphate, do not interfere in amounts up to at least 100 ppm.

It is to be noted that using the dilution technique a ten-fold decrease of any interfering substances is obtained (on a 1·0-ml sample), and it is thus possible that relatively high concentrations of ions in a *raw* sample may be tolerated without any noticeable loss in accuracy.

Procedures for the decomposition of complex cyanides to give hydrogen cyanide for determination have been previously reviewed[8,9] and any of the recommended methods are applicable to the determination of cyanide by *p*-phenylenediamine.

Stability of the Reagent

The stability of the reagent was investigated using standard solutions of cyanide (4-ml samples) and a 0·2% w/v solution of *p*-phenylenediamine in 0·5*M* hydrochloric acid:

(1) freshly prepared (less than 1 hr)
(2) solution kept in a 'dark' bottle for 6 weeks.

TABLE VII(a).—ABSORBANCE OF REAGENT BLANK SOLUTION

Time after mixing, *min*	15	25	30
Absorbance (fresh solution)	0·019	0·020	0·022
Absorbance (6-weeks old solution)	0·021	0·020	0·023

TABLE VII(b).—ABSORBANCE OF SOLUTIONS CONTAINING CYANIDE

Cyanide, *ppm*	Time after mixing, *min*	Absorbance (corrected for blank)	
		Aged reagent	Fresh reagent
0·2	15	0·200	0·196
	25	0·203	0·201
	30	0·203	0·201
0·4	15	0·398	0·396
	25	0·406	0·404
	30	0·406	0·404
2·0	15	2·01	2·01
	25	2·01	2·02
	30	2·02	2·03

From the results in Tables VII(a) and VII(b), the reagent solution is stable for at least 6 weeks when stored in a dark bottle, and the reproducibility of the results at 30 min after mixing is ±1%.

CONCLUSION

The procedure to be used depends on the expected concentration of cyanide to be determined, the size of the sample available and the contaminants. The following procedures are recommended.

Unlimited sample ($\nless$ 40 ml)

For a concentration of cyanide between 0·005 and 0·25 ppm, the sample is obtained free from interferences (if necessary) by distillation, aeration, *etc.* Forty ml of the sample are then treated with 2·0 ml of saturated bromine water and 0·1 ml of concentrated hydrochloric acid and the solutions thoroughly mixed. After 5 min, 0·4 ml of arsenious acid solution is added and the total volume adjusted to 50·0 ml. A 5·0-ml aliquot of the mixture is then treated with 4·0 ml of freshly mixed pyridine/*p*-phenylenediamine (3·0 ml of pyridine reagent + 1·0 ml of *p*-phenylenediamine solution). After thorough mixing and standing for 30 min at room temperature, the absorbance of the resulting solution is compared to that of water at 515 mμ.

The absorbance of a blank solution should be determined under the same conditions and the absolute absorbance used to calculate the concentration of cyanide present, from a previously determined calibration curve.

For samples containing 0·25—100 ppm of cyanide, a suitable aliquot should first be diluted to 40·0 ml with cyanide-free water, then processed as above.

Limited Sample

If the sample size is limited and dilution to 40·0 ml would decrease the concentration below 0·005 ppm, then 4·0 ml of the sample are mixed well with 0·2 ml of saturated bromine water and 0·1 ml of concentrated hydrochloric acid. After 5 min, 0·2 ml of arsenious acid solution is added, followed by 4·0 ml of freshly mixed pyridine/*p*-phenylenediamine. After 30 min at room temperature, the absorbance is measured at 515 mμ.

A separate calibration curve should be determined. If necessary, the sample may be obtained free from interferences as above.

Zusammenfassung—Zur Bestimmung von Cyanidspuren in Wässern wird p-Phenylendiamin in einer Reaktion vom Typ der König-Reaktion verwendet. Mit geringfügigen methodischen Änderungen läßt sich die Methode im Bereich von 0,005 bis 100 ppm anwenden.

Résumé—Pour doser le cyanure à l'état de traces dans les eaux, on utilise la p-phénylènediamine, dans une réaction du type König. Avec une légère modification de technique, la méthode est applicable dans l'intervalle de 0,005 à 100 p.p.m.

REFERENCES

[1] W. N. Aldridge, *Analyst*, 1944, **69**, 262; 1945, **70**, 474.
[2] J. Epstein, *Analyt. Chem.*, 1947, **19**, 272.
[3] W. König, *J. prakt. Chem.*, 1904, **69**, 105; *Z. Angew. Chem.*, 1905, 115.
[4] L. S. Bark and H. G. Higson, *Talanta*, 1964, **11**, 471.
[5] *Idem*, *Analyst*, in press.
[6] M. O. Baker, R. A. Foster, B. G. Post and T. A. Hiett, *Analyt. Chem.*, 1955, **27**, 448.
[7] I. Nusbaum and P. Skupeko, *Sewage Ind. Wastes*, 1951, **23**, 875.
[8] L. S. Bark, *Ind. Chemist*, 1962, 525.
[9] L. S. Bark and H. G. Higson, *Analyst*, 1963, **88**, 751.

Talanta, 1964, Vol. 11, pp. 633 to 640. Pergamon Press Ltd. Printed in Northern Ireland

WET OXIDATION OF ORGANIC COMPOSITIONS

MIXED NITRIC AND HYDROCHLORIC ACIDS WITH AMMONIUM PERCHLORATE AS OXYGEN DONORS

G. FREDERICK SMITH
Noyes Chemical Laboratories, University of Illinois, Urbana, Illinois, U.S.A.

(*Received* 14 *October* 1963. *Accepted* 23 *October* 1963)

Summary—The wet oxidation of organic compositions as introductory manipulation in the determination of micro- and macrogram metallic and non-metallic elements is described. The principal oxygen donor in this procedure is perchloric acid generated *in situ*. Mixed nitric and hydrochloric acids are employed to convert ammonium perchlorate to perchloric acid. The three mixed acids then serve as superior solvent for the organic matter to be oxidised. Conditions are particularly suited for the oxidation of large samples. Reaction rates are repressively controlled to give assurance against violent oxidation. Applications include organic compositions, essentially of cellulose, sugars and polyhydric alcohols, or proteins. Conditions prevail in the leisurely application of reaction time to provide maximum effects from nitric acid. This provision is the key to slowly advancing oxidation potential. The final high potential provided by perchloric acid over the temperature range 150° to 203°, stepwise increasing, completes oxidations with no accompanying menacing carbonisations. Reaction times involve 50 to 60-min digestions.

INTRODUCTION

THE oxidation of organic compositions by dry ignition has been shown[1] to be frequently accompanied by a serious loss of residual elements from high temperature volatilisation. By exhaustive test, wet oxidations employing perchloric, sulphuric and nitric acids involve no loss under easily adjusted reaction conditions. There appears to be general acceptance that the use of perchloric acid as oxygen donor in wet oxidation of organic compositions provides the most valuable reaction medium.

Wet oxidation digestions in the elimination of organic matter, with retention of metallic and non-metallic accompanying elements, fall into five general categories according to the reagents involved:

(1) Nitric plus perchloric acids: "The Liquid Fire Reaction."[2]

(2) Perchloric acid alone. This procedure applies static oxidation potential magnitudes of predetermined values.[3]

(3) Perchloric and sulphuric acid mixtures. This application applies high redox potentials.[4]

(4) Sulphuric acid at 350° followed by a perchloric acid finishing reaction at 190–195°.[5] Used with fuel oils and samples rich in fat.

(5) Periodic acid and perchloric acid: "The Periodic Acid Liquid Fire Reaction."[6]

The last listed method provides general oxidation at the lowest possible temperatures and shortest reaction times.

Employing one or more of these five reaction procedures, a wide range of organic compositions may be expeditiously oxidised. Samples include fuels (such as coal or oils), carbon (such as gas-mask canister materials), fats, synthetic fabrics (such as nylon, orlon or dacron), foods and feeds, leather and wool, syrups, conserves, fruits and cellulose-rich products. Method (5) has been applied to the determination of amino nitrogen.[7] Many published works involving one or more of the five procedures have been documented, but these are too numerous to cite in the interests of brevity.

EXPERIMENTAL

Reagents

Concentrated (67–68%) *nitric and* (37–38%) *hydrochloric acids*

Ammonium perchlorate (99·5%). As produced in multiple tonnage for use in the solid rocket fuel programme. Recrystallisation purification is recommended.

Apparatus

The Bethge apparatus[8] is requisite. By its use reaction conditions are best controlled. Heat is provided using a ring burner and modified nichrome wire gauze. A modified Rogers ring burner with micro control of gas-fuel intake[9] is preferred. An electric hot plate or a glass fabric heating mantle with voltage control may be substituted. Rate of energy input should be of such magnitude as to bring the reaction temperature to no more than 100° during the first 5 min. The Bethge apparatus assembled is shown in Fig. 1. Adjustment of the thermometer insert is provided by a teflon adapter as shown.

RESULTS AND DISCUSSION

Reaction characteristics

The reactions involved fall under three stages:

(A) Initial conversion of ammonium perchlorate to perchloric acid. The reaction with mixed hydrochloric and nitric acid converts the ammonium ion to nitrous oxide and water. An amount of water approximately equal to the combined mixed acid volumes is added to the sampling mixture. Reaction time is 10 min at a maximum of 110°. Heat is applied at such magnitude to attain 90° to 100° in not less than 5 min. Reaction conditions involve a mildly exothermic condition and the reaction is conducted under reflux of the condensed vapour phase. In general, the organic compositions being oxidised are dissolved by the three mixed acids present during stage (A).

(B) Adjustment is provided to retain condensate during the remainder of the digestion. The hydrochloric acid has been consumed. The dilute solution of mixed nitric and perchloric acids gradually concentrates over the temperature range 110° to 150°. The reaction is exothermic to a greater or less extent depending upon the nature of the organic matter being oxidised. During this stage the nitric acid undergoes gradual uniform increase in concentration. The oxidation potential of the nitric acid increases gradually to its maximum value at 150°. All organic matter capable of destruction by nitric acid has been reacted upon and excess nitric acid has been collected in the condensate. Little reactivity from perchloric acid has, as yet, been applied. Stage (B) requires from 30 to 40 min at the same application of heat applied throughout the three stages (A), (B) and (C). Variation in time during stage (B) is governed by the exothermic reaction provided by nitric acid oxidation.

(C) The final stage completes the oxidation following the limited destruction of organic matter provided by nitric acid and elimination of its excess at 140° to 150°. At 150° the first influence of perchloric acid as oxygen donor becomes effective. As the temperature advances because of concentration increase, the oxidation potential steadily and uniformly increases from approximately 0·8 to 2·0 V. The perchloric acid concentration increases from 50% at 150° to 72·5% at 203°. The reaction over this range becomes increasingly exothermic. At 203° the distillate and residual acid

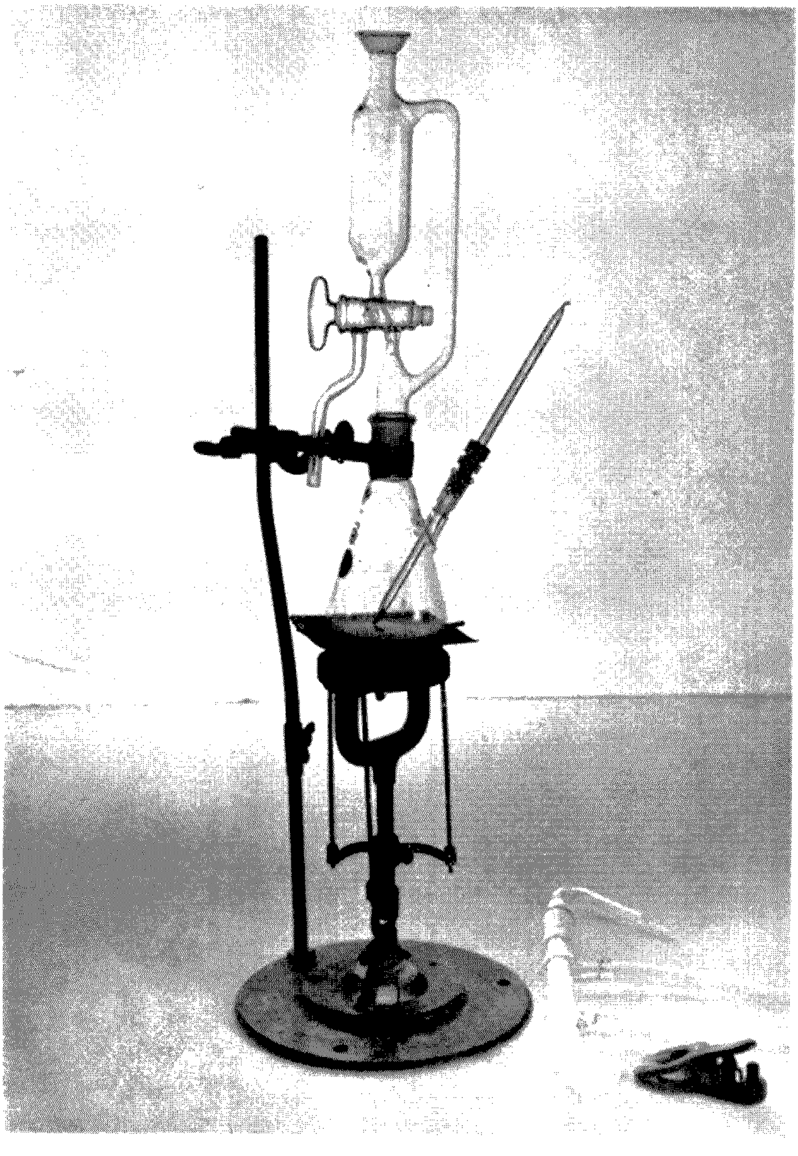


FIG. 1.—Bethge apparatus (water condenser disengaged) and modified Rogers ring burner.

in the reaction flask is at the water-perchloric acid azeotropic composition. The extent of the exothermic reaction depends upon the nature of the organic material being oxidised. Stage (C) requires 10 min, in general. Total reaction time, over-all, is approximately 60 min.

Reaction advantages

Previously described wet oxidation procedures[2–6] have one common objective, that of controlled oxidation at minimum time intervals. All types of organic compositions may be oxidised by one to three of the various applicable procedures. In general, the products oxidised involve little or no carbonisation. Degradation products, as well as the original compositions, are usually all in homogeneous solution throughout the entire digestion. Such reactions, if accompanied by the formation of dark brown or black reaction products, are still reaction rate controlled. However, in general, sample weights are limited to the 1 to 2 g magnitude.

The present work involves no reactions resulting in dark or black reaction media. Samples of 5 g are applicable. Conditions are adjusted to require longer reaction periods. Accordingly, the full possible effect of nitric acid as oxygen donor is provided. The oxidation of organic matter is thus as complete as possible before the perchloric acid oxidation begins. By following the reaction temperature during stage (b), the mildly exothermic nitric acid oxidation indicates the extent to which the removal of organic matter is progressing. Adjustment in the volume of nitric acid employed may then be made. Perchloric acid reaction in stage (c) may thus be favourably minimised.

The entire new procedure requires little operator attention. The apparatus involved is readily assembled and dismantled. It does not require a fume hood. The use of the new procedure encourages those reluctant to apply perchloric acid in wet oxidations, in fear of uncontrolled reaction intensities, to adopt the procedure in routine operations. In the present studies, no protective reaction screen was employed in any test oxidation.

Graphical representation of data

Three distinct types of organic compositions for wet oxidation include those which are predominantly cellulose, sugars or proteins. The time-temperature recording of the progress of the oxidation is the most informative technique serving to characterise each type of reaction. Employing the Bethge apparatus (Fig. 1), the oxidation of 2 g of tuna fish is characterised in Fig. 2. Because of the small weight of sample the reaction flask employed is 250 ml in volume. The oxidation is, for this reason, complete in 26 min. Stage (A) in Fig. 2 is complete in 6 min, and from 4 to 6 min no temperature rise indicates the conversion of ammonium perchlorate to perchloric acid. The sample during this period has been completely dissolved. At this point the return of reflux to the reaction flask is discontinued. For the following 16 min the stage (B) reaction of nitric acid is operative. Over the period 6 to 14 min the temperature elevation is slow and uniform indicating no appreciable exothermic nitric acid oxidation. Over the reaction period 15 to 22 min the oxidation is progressing at an increased tempo, as shown by the materially increased slope of the time-temperature plot. At 22 min the temperature has advanced to 150°. All excess nitric acid has now left the reaction flask to be collected in the condenser system. The effective oxidation period, 22 to 26 min, involves the reaction of perchloric acid as oxygen donor, stage (C). At 150° the perchloric acid concentration is approximately 50%. Here there comes into play a gradual increase in oxidation potential accompanied by a material exothermic reaction complete in 4 min. The completion of oxidation (as indicated by the oxidation of the chromium indicator,* Cr^{III} to Cr^{VI}, at 202°) indicates a perchloric acid concentration

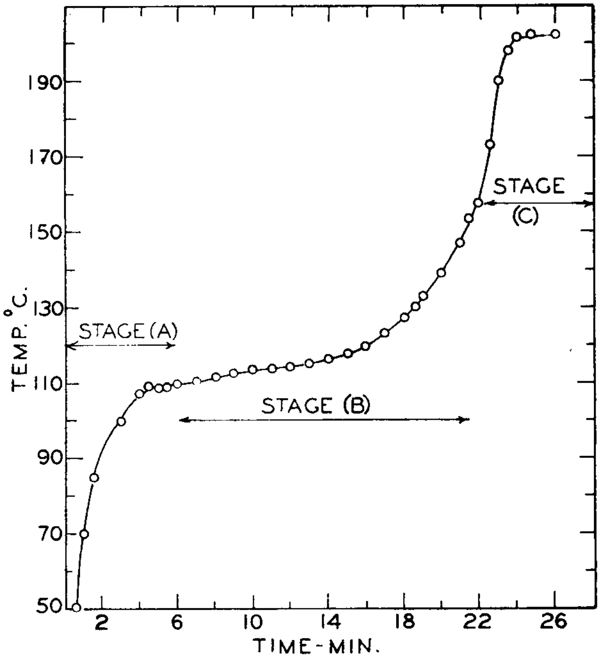


FIG. 2.—Oxidation of tuna fish [2 g of sample; 250-ml reaction flask; 10 ml of HCl; 17·6 ml of HNO_3; 21·5 g of NH_4ClO_4; 26 ml of H_2O; chromium indicator; 43 ml of distillate; 21·75 g (13 ml) of residue in $HClO_4$ flask].

of 72·5%. During the entire reaction [stages (A), (B) and (C)] no alteration of heat applied has been made. Stage (C) owes its temperature rise almost entirely to its exothermic properties.

At the completion of the oxidation the condensate may be removed, the air and water-cooled condenser rinsed and the distillation continued with elevation of temperature input. By this means excess perchloric acid can be removed from the reaction flask. Any silica originally present in the sample is now dehydrated and insoluble. The reaction flask can now be diluted with water, filtered and made ready for determination of metallic and non-metallic minor or major components originally present in the organic compositions of the sample. The flask contents, after completion of the oxidation covered by the results of Fig. 2, weighed 21·75 g or approximately 13 ml of perchloric acid. The distillate was 43 ml.

Non-condensed volatile products may be conducted from the top of the water-cooled condenser by flexible tubing into the sink drain, thus avoiding, by the use of the Bethge apparatus, the need for a fume hood in which to perform the oxidation.

---

* 1–2 mg of potassium dichromate are included in the reaction mixture. As long as any organic matter is present, the chromium is held in the green tervalent state. When all traces of organic matter are oxidised, the chromium is immediately oxidised to the orange hexavalent state.

Oxidation of 5-g samples of organic compositions

The oxidation of 5 g of dried beef is characterised in Fig. 3. A 1000-ml Bethge apparatus was employed. As well as using a 5-g sample, the reactants were augmented and a resultant 60-min reaction time was required. As could be predicted, the general profile of the graphical recording of data duplicates that of Fig. 2 for the reason that both organic compositions oxidised are proteins (distillate: 67 ml; perchloric acid remaining in the reaction flask: 33·6 g or 20 ml).

The oxidation of 5 g of vegetable tanned leather is graphically recorded in Fig. 4. The reaction time is shown as 41 min under the same conditions as for an equal sample of dried beef. In the case of leather it is observed that the oxidation is less in

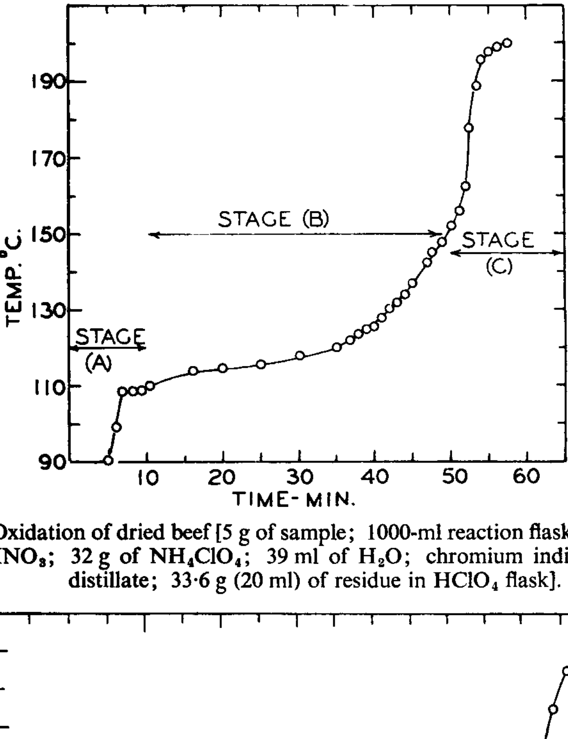


Fig. 3.—Oxidation of dried beef [5 g of sample; 1000-ml reaction flask; 15 ml of HCl; 26·5 ml HNO_3; 32 g of NH_4ClO_4; 39 ml of H_2O; chromium indicator; 67 ml of distillate; 33·6 g (20 ml) of residue in $HClO_4$ flask].

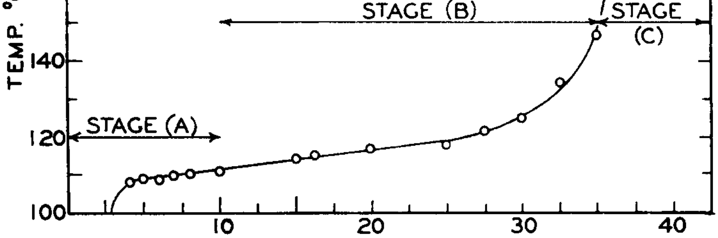


Fig. 4.—Oxidation of leather [5 g of sample; 500 or 1000-ml reaction flask; 15 ml of HCl; 35 ml of HNO_3; 32 g of NH_4ClO_4; 39 ml H_2O; chromium indicator; 71 ml of distillate; 29 g (17·4 ml) of residue in $HClO_4$ flask].

the nitric acid stage (B) and the burden of reactivity is placed upon the perchloric acid stage (C). With the same sample weight, the distillate was 71 ml and the perchloric acid in the reaction flask 29 g or 17·4 ml. The same amounts of mixed reactants were employed in the reactions shown in Figs. 3 and 4. An additional 2·6 ml of perchloric acid were consumed.

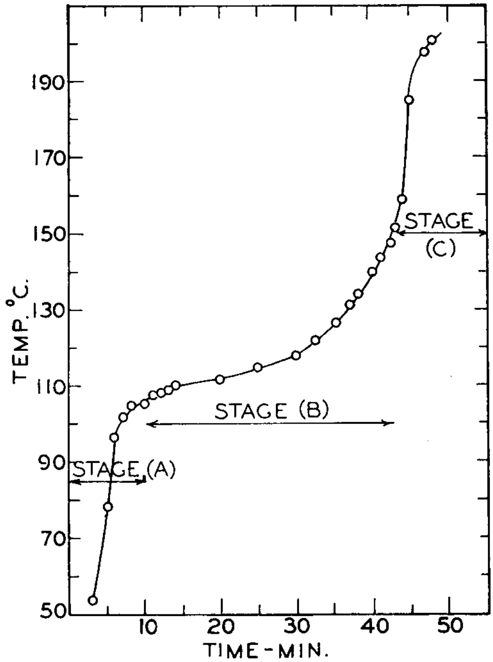


FIG. 5.—Oxidation of sugar [5 g of sample; 1000-ml reaction flask; 15 ml of HCl; 35 ml of HNO_3; 32 g of NH_4ClO_4; 39 ml of H_2O; chromium indicator; 70 ml of distillate; 35·3 g (21·1 ml) of residue in $HClO_4$ flask].

The oxidation of 5 g of cane sugar is shown in the graph of results in Fig. 5. The results indicate that the oxygen donor contribution of both nitric acid and perchloric acid are approximately equal.

The oxidation of 5 g of raffia and 5 g of cinnamon bark (principally both cellulose) is depicted in Figs. 6 and 7. As would be predicted, the results indicate almost duplicate reaction characteristics. Subsequent to the reaction with nitric acid in stage (B), the exothermic nature of the perchloric acid oxidation is more pronounced than that of either the oxidation of samples essentially sugar or protein in composition.

Reaction commentary

Nitrous oxide formed in reaction stage (A), being soluble in water and many organic compositions, especially in the case of cellulose-laden materials, promotes foam formation. Such foams are very light and can be counteracted by increasing the flask volume of the Bethge apparatus.

The oxidations described in Figs. 2 to 7 may be well conditioned by employing modified amounts of reactants to suit any particular type of routine plant control oxidation samples. By trial, for example, the volume of nitric acid may be reduced to such favourable volume, provided there results no dark brown or black degradation reaction products. The time required may thus be favourably reduced for a given application.

Sufficient perchloric acid should be obtained to prevent dry spots from forming on the inside bottom of the reaction flask. By withdrawing distillate from the apparatus condenser system, and rinsing with distilled water at the completion of oxidations, one may collect by further distillation the bulk of the perchloric acid formed previously.

Organic compositions containing siliceous materials, in boiling 72·5 % perchloric acid, precipitate insoluble SiO_2 quantitatively. In general, perchloric acid is a preferred medium for final determination of metallic and non-metallic residual isolated

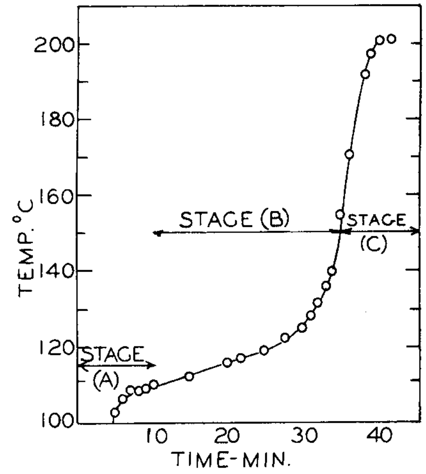


FIG. 6.—Oxidation of raffia [5 g of sample; 1000-ml reaction flask; 15 ml of HCl; 35 ml of HNO_3; 32 g of NH_4ClO_4; 39 ml of H_2O; chromium indicator; 71 ml of distillate; 29 g (17·4 ml) of residue in $HClO_4$ flask].

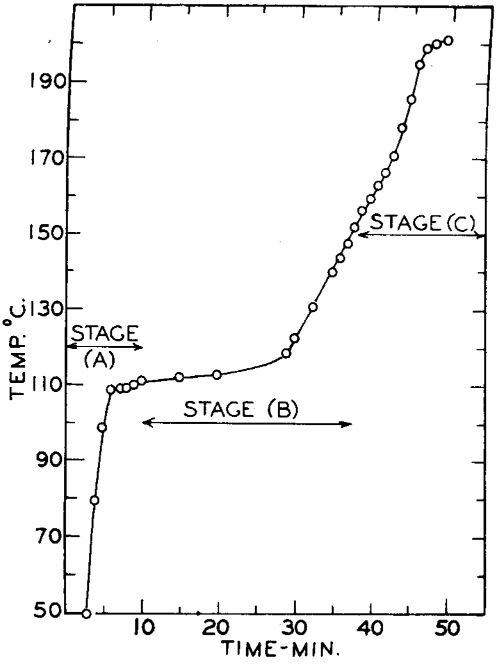


FIG. 7.—Oxidation of cinnamon bark [5 g of sample; 1000-ml reaction flask; 15 ml of HCl; 35 ml of HNO_3; 32 g of NH_4ClO_4; 39 ml of H_2O; chromium indicator; 73 ml of distillate].

and retained elements. If for any reason a sulphuric acid solution is preferred, it may be added to the perchloric acid solution and the latter displaced by volatilisation upon fuming at 180–190°.

Forty test oxidations of a wide variety of organic compositions have been carried out. Analysts, formerly apprehensive of methods 2 to 6, may well make "assurance doubly sure" through the use of the present disclosures.

Zusammenfassung—Die nasse Oxydation organischer Mischungen als erste Operation bei der Bestimmung von Mikro- und Makromengen metallischer und nicht-metallischer Elemente wird beschrieben. Bei diesem Vorgang dient in situ erzeugte Überchlorsäure in erster Linie als Sauerstoffquelle. Mit Salpetersäure-Salzsäure-Gemisch wird Ammoniumperchlorat zu Überchlorsäure umgesetzt. Das Dreisäurengemisch dient dann als ausgezeichnetes Lösungsmittel für das zu oxydierende organische Material. Die Bedingungen sind besonders zur Oxydation großer Proben geeignet. Die Reaktionsgeschwindigkeit wird zum Schutz gegen zu heftige Oxydation unter Kontrolle gehalten. Die Anwendungen schließen hauptsächlich Mischungen von Cellulose, Zuckern, mehrwertigen Alkoholen oder Proteinen ein. Hauptsächlich kommt es darauf an, daß man der Reaktion Zeit läßt, damit die Salpetersäure optimal ausgenutzt wird. So kann man das Oxydationspotential langsam steigern. Das zum Schluß von Überchlorsäure bei stufenweise ansteigender Temperatur von 150° bis 203° gelieferte hohe Potential beendet, die Reaktion, ohne daß Verkohlung droht. Der Aufschluß dauert 50–60 Minuten.

Résumé—On décrit l'oxydation humide de mélanges organiques, en tant que manipulation initiale dans le dosage d'éléments métalliques et non métalliques aux échelles du microgramme et du macrogramme. Le principe donneur d'oxygène est, dans cette technique, l'acide perchlorique généré "in situ". On utilise un mélange d'acides nitrique et chlorhydrique pour convertir le perchlorate d'ammonium en acide perchlorique. Le mélange des trois acides sert alors de solvant principal pour la matière organique à oxyder. Les conditions sont particulièrement appropriées à l'oxydation de grosses prises d'essai. Les vitesses de réaction sont très étroitement controlées, afin que l'on soit assuré d'éviter une oxydation violente. Les applications comprennent des mélanges organiques constitués essentiellement de cellulose, de sucres et polyols, ou de protéines. Les conditions reposent essentiellement sur un temps de réaction suffisamment long pour obtenir les effets maximaux de l'acide nitrique. Cette précaution est la clef qui autorise un potentiel d'oxydation lentement progressif. Le haut potentiel final apporté par l'acide perchlorique, pour les températures s'échelonnant de 150° à 203°, et croissant graduellement, complète les oxydations sans que celles-ci soient accompagnées d'une menace de carbonisation. Les temps de réaction comprennent des digestions de 50–60 minutes.

REFERENCES

[1] J. Pijck, J. Gillis and J. Hoste, *Internat. J. Appl. Radiation Isotopes*, 1961, **10**, 149; *Chem. Abs.*, 1961, **55**, 23650.
[2] G. F. Smith, *Analyt. Chim. Acta*, 1953, **8**, 397.
[3] *Idem, ibid.*, 1947, **17**, 175.
[4] H. Diehl and G. F. Smith, *Talanta*, 1959, **2**, 209.
[5] *Idem, ibid.*, 1959, **3**, 41.
[6] *Idem, ibid.*, 1960, **4**, 185.
[7] L. B. Moore and Harvey Diehl, *Analyt. Chem.*, 1962, **34**, 1638.
[8] Reference 6 above: photo reproduction in Fig. 1.
[9] Illustrated in Fig. 1.

Talanta, 1964, Vol. 11, pp. 641 to 646. Pergamon Press Ltd. Printed in Northern Ireland

5-(8-HYDROXY-5-QUINOLYLMETHYL)-8-HYDROXY-1-METHYLQUINOLINIUM SALTS AS SOLVATOCHROMIC CHELATING AGENTS

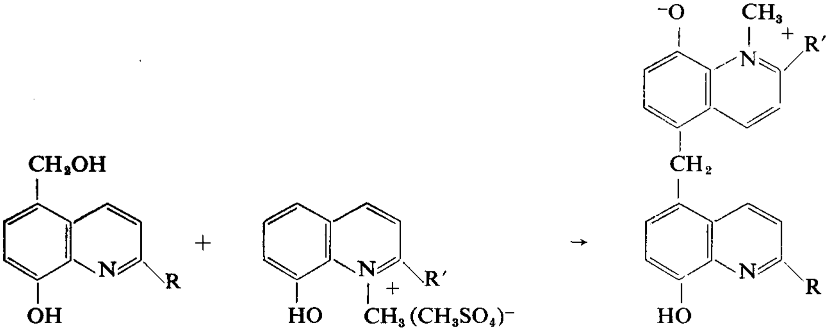
J. W. Faller and J. P. Phillips
Department of Chemistry, University of Louisville, Louisville 8, Kentucky, U.S.A.

(*Received* 25 *October* 1963. *Accepted* 29 *November* 1963)

Summary—The title compounds and related substances were prepared, characterised and tested as solvatochromic chelating agents. These reagents show large color changes with solvent, and the chelates, though insoluble in most common solvents, are also solvatochromic. Reagents with a 2-methyl group adjacent to the chelating centre do not precipitate aluminium, and this effect can be used as a colour test for aluminium.

In continuation of studies of chelating agents that undergo large colour changes with solvent polarity (solvatochromism),[1] we have prepared four reagents of general formula I (R and R′ are H or CH_3). In these compounds the solvatochromism is conferred by the betaine function in one quinoline ring, and this is isolated by a methylene bridge from an 8-quinolinol (or 8-hydroxyquinaldine) moiety that can form chelates with metal ions. The chelates as well as the reagents can thus be solvatochromic, and it was anticipated that the two functions should be independent.

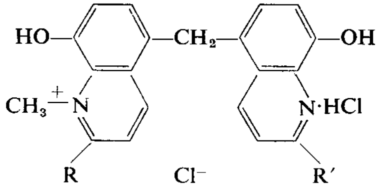
It was not possible to obtain the compounds by direct methylation of available bis(8-hydroxy-5-quinolyl)methanes[2,3] because dimethyl sulphate methylated both nitrogen atoms (see *Experimental*); though these products are solvatochromic they obviously are not chelating agents. The desired monomethylated compounds were obtained by rather tedious condensation reactions of 5-hydroxymethyl-8-quinolinol[4] or 5-hydroxymethyl-8-hydroxyquinaldine[5] with either 1-methyl-8-hydroxyquinolinium methosulphate or its 2-methyl derivative as shown in the following equation:



I
(R = R′ = H)
(II–IV; R or R′ is H or Me)

A similar condensation of 1-methyl-5-hydroxymethyl-8-hydroxyquinolinium methosulphate with 8-quinolinol also gave I, identical in m.p. and ultraviolet-visible spectra with a sample of the same compound prepared by the above reaction. All four of the compounds were isolated as the dark red inner salt represented by formula I and were also converted to the dihydrochlorides, yellow solids of high decomposition point. It is noteworthy (Table I) that all products were hydrated, a demonstration of the affinity of these substances for solvent molecules.

TABLE I.—5-(8-HYDROXY-5-QUINOLYLMETHYL)-8-HYDROXY-1-METHYLQUINOLINIUM SALTS



Substituents in formula						Nitrogen	
No.	R	R′	Formula	M.P.,[a] °C	Yield, %	Calcd., %	Found, %
I	H	H	$C_{20}H_{18}Cl_2N_2O_2 \cdot H_2O$	c320	—	6·87	6·81
IB[b]			$C_{20}H_{16}N_2O_2 \cdot H_2O$	185	88	8·38	8·38
II	CH_3	CH_3	$C_{22}H_{22}Cl_2N_2O_2 \cdot H_2O$	238	—	6·44	6·41
IIB[b]			$C_{22}H_{20}N_2O_2 \cdot H_2O$	187–189	94	7·73	7·57
III	H	CH_3	$C_{21}H_{20}Cl_2N_2O_2 \cdot H_2O$	233	—	6·65	6·68
IIIB[b]			$C_{21}H_{18}N_2O_2 \cdot H_2O$	225	93	8·04	8·24
IV	CH_3	H	$C_{21}H_{20}Cl_2N_2O_2 \cdot H_2O$	207–209	—	6·65	6·50
IVB[b]			$C_{21}H_{18}N_2O_2 \cdot H_2O$	155	61	8·04	8·42

[a] All compounds melt with decomposition.

[b] B = Betaine, which refers to the neutral molecule formed by the loss of two HCl molecules from the salt (see equation).

Spectra of basic I in a variety of solvents showed a considerable negative solvatochromism in the visible (Table II), with a change in the wavelength of principal maximum by over 100 mμ from water to chloroform as solvent. [For comparative purposes maxima for the inner salt (V) of *N*-methyl-8-hydroxyquinaldinium hydroxide are listed too.] The spectrophotometric determination of ionisation constants of these compounds gave the results of Table III, with the three ionisation constants representing transitions, respectively, from diprotonated to neutral (zwitter-ionic) to anion forms as the pH increases. Thus, the first pKa is for the N-H$^+$ dissociation and the second and third for the phenolic hydrogen atoms. Comparative figures for some related compounds are also listed.

Infrared spectra of potassium bromide pellets of the compounds were also obtained.

Because all four reagents have a pK_2 of about 6·7 they would be expected to exist primarily in the cationic form at pH values of 5 or less, and chelates formed at pH 5 or less should not be solvatochromic. All reagents gave yellow solutions at pH 5 with copper, nickel, zinc and aluminium ions and a green solution with iron^{III} ion. In concentrated solutions precipitates of these chelates, presumably as salts with anions in the solution, could be obtained, but lack of knowledge of the anions incorporated prevented successful analysis.

At pH 9 orange to red precipitates from aqueous solution were obtained with copper, cobalt, nickel, zinc, magnesium and iron^{III} ions using reagents I–IV and with aluminium using reagents I and IV. The reagents are soluble in chloroform, but the chelates

TABLE II.—ABSORPTION MAXIMA IN THE VISIBLE SPECTRA OF I AND V

Solvent[a]	Dielectric constant[b] (and Z values[c])	Maximum, $m\mu$ (log ε)	
		I	I
Water	80·4 (94·6)	458 (3·30)	428 (3.18)
90% MeOH	37·9 (85·8)	496 (3·26)	456 (3·06)
90% 1-Propanol	29·8	504 (3·25)	465 (3·13)
90% 2-Propanol	23·5 (83·20)	507 (3·24)	470 (3·09)
90% Acetone	25·9 (77·7)	516 (3·24)	479 (3·09)
Benzyl alcohol	13·1	495 (3·29)	462 (3·18)
Chloroform	4·8 (63·2)	575 (3·39)	529 (3·09)
80% 2-Propanol[d]	29·7	499 (3·25)	463 (3·12)
60% 2-Propanol[d]	45·6	487 (3·27)	456 (3·13)
40% 2-Propanol[d]	57·3	481 (3·28)	449 (3·14)
20% 2-Propanol[d]	68·1	472 (3·30)	438 (3·16)

[a] All aqueous solutions were also 0·01*M* in ammonia. Percentages are volume percentages at 30°, the temperature of measurement.

[b] Dielectric constants of aqueous solutions were interpolated from the values of G. Akerloeff, *J. Amer. Chem. Soc.*, 1932, **54**, 4125; 1936, **58**, 1241.

[c] These measures of solvent polarity were interpolated from the values of E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253.

[d] Results at 10% intervals for 2-propanol-water mixtures were recorded; there is a uniform negative solvatochromic effect in this series as a function of dielectric constant.

TABLE III.—ACID DISSOCIATION CONSTANTS OF 5-(8-HYDROXY-5-QUINOLYLMETHYL)-8-HYDROXY-1-METHYLQUINOLINIUM COMPOUNDS

Compound No.	pK_1	pK_2	pK_3
8-Quinolinol[a]	5·13	—	9·89
I	4·6	6·70	9·85
III	4·7	6·62	10·2
V	—	6·83	—

[a] S. F. Mason, *J. Chem. Soc.*, 1958, 674.

TABLE IV.—ULTRAVIOLET-VISIBLE ABSORPTION MAXIMA

Compound	0·1*M* HCl	0·1*M* KOH	pH 7·9[a]
I	257 (4·81), 380 (3·70)	258 (4·57), 275 (4·53) 357 (3·74), 458s (3·32)	462 (3·29)
II	261 (4·97), 370 (3·73)	262 (4·58), 281 (4·55), 440s (3·31)[b]	441 (3·28)
III	260 (4·95), 377 (3·72)	263 (4·64), 275s (4·60), 355 (3·81), 464 (3·34)	465 (3·34)
IV	358 (4·87), 371 (3·75)	257 (4·53), 281 (4·48), 445s (3·30)[b]	447 (3·22)
V	258 (4·73), 357 (3·41)	277 (4·66), 432 (3·25)	

[a] Visible maxima only.

[b] An additional maximum is present near 355 mμ; this maximum appears to be caused by the chelating function.

are not. This lack of solubility of the chelates extended to most organic solvents, though aqueous pyridine mixtures did dissolve them well enough to allow solvatochromism to be observed, the chelates ranging from orange to violet with increasing pyridine content. In water the chelates were somewhat more soluble than is suitable for quantitative precipitations.

It would appear that the solvatochromism of the reagent determines in large part the colour of the chelates. Chelates prepared in alcohols and other non-aqueous solvents showed colours generally close to that of the reagent in each solvent, but upon filtration and loss of solvent the chelates changed to the red colour usually observed in the samples prepared from water solutions.

Any utility of these reagents must rest on the colours produced by extraction of the reagent. A novel colour test for aluminium, for example, is afforded by adding III to an aqueous solution containing metal ions to chelate all except aluminium; after addition of base, chloroform then extracts any excess III. Addition of a drop of dilute I to the aqueous phase and extraction again with chloroform will give a blue-violet chloroform layer if no aluminium is present but will leave the chloroform colourless if aluminium is present, because the aluminium chelate of I is not soluble in chloroform. There is no chelate of III with aluminium.

EXPERIMENTAL

Preparation of Compounds

1-Methyl-8-hydroxyquinolinium methosulphate was obtained by heating 0·1 mole of 8-quinolinol until liquid, then adding 0·1 mole of dimethyl sulphate and heating the mixture with stirring in a steam bath for 10 min. The solid product was washed with ether, dissolved in 2-propanol and precipitated with ether, and finally recrystallised from 2-propanol as yellow needles of m.p. 156° (52% yield). (Literature[6] gives m.p. 145–6°.)

1-Methyl-8-hydroxyquinaldinium methosulphate (m.p. 169–70°) was prepared similarly in 53% yield from 8-hydroxyquinaldine. (*Analysis.* Calcd. for $C_{12}H_{15}NO_6S$: C, 50·51; H, 53·0; N, 4·91. Found: C, 50·56; H; 4·89; N, 4·78.)

An aqueous solution of the methosulphate was converted to the chloride by passage through Dowex 2X-8 in the chloride form, evaporation of the effluent and recrystallization from 90% 2-propanol in the form of yellow needles melting at 231°. (*Analysis.* Calcd. for $C_{11}H_{12}ClNO{\cdot}2H_2O$: N, 5·48. Found: N, 5·48.)

1-Methyl-5-hydroxymethyl-8-hydroxyquinolinium methosulphate was similarly obtained from 5-hydroxymethyl-8-quinolinol[4] and dimethylsulphate in 73% yield by heating a nitrobenzene solution of the reactants for 1 hr on the steam bath. After three recrystallisations from 90% 2-propanol the product melted at 128°. (*Analysis.* Calcd. for $C_{12}H_{15}NO_6S{\cdot}H_2O$: N, 4·39. Found: N, 4·35.) In 0·1*M* hydrochloric acid the compound had λ_{max} 376 mμ; in 0·1*M* potassium hydroxide, 470 mμ (log ε 2·8).

5,5′-Methylenebis(8-hydroxy-1-methylquinolinium) dimethosulphate, decomposing 211–215°, was prepared in 47% yield by heating bis(8-hydroxy-5-quinolyl)-methane in excess dimethyl sulphate for 1 hr on the steam bath, precipitating the product by addition of 1 : 1 acetone-ether and recrystallising from 2-propanol. (*Analysis.* Calcd. for $C_{23}H_{26}N_2O_{10}S_2$: C, 49·81; H, 4·73; N, 5·05. Found: C, 49·78; H, 4·98; N, 5·02.)

This compound was converted to the dichloride, decomposing at 300°, by extracting an ammoniacal solution (pH 10) with amyl alcohol, adding ether and extracting the resulting solution with 0·1*M* hydrochloric acid. Evaporation of the aqueous extract and recrystallisation from ethanol gave the dichloride. (*Analysis.* Calcd. for $C_{21}H_{20}Cl_2N_2O_2{\cdot}2H_2O$: N, 6·38. Found: N, 6·31.)

In a similar way bis(8-hydroxy-5-quinaldyl)methane[3] was converted to the dimethylated derivative, isolated only as the chloride (m.p. 250°), because the methosulphate was hygroscopic. (*Analysis.* Calcd. for $C_{23}H_{24}Cl_2N_2O_2$: N, 6·46. Found: N, 6·43.)

5-(8-*Hydroxy-5-quinolylmethyl*)-8-*hydroxy*-1-*methylquinolinium salts*

Either 0·01 mole of 5-hydroxymethyl-8-quinolinol (1·75 g) or 5-hydroxymethyl-8-quinaldinol (1·89 g) or 5-hydroxymethyl-8-quinaldinol (1·89 g) and 0·02 mole of 1-methyl-8-hydroxy-quinolinium methosulphate (5·43 g) or 1-methyl-8-hydroxyquinaldinium methosulphate (5·71 g) were dissolved in 20 ml of glacial acetic acid. After the dropwise addition of 6 ml of concentrated sulphuric acid, the reaction mixture was allowed to stand for 2 days at room temperature, then was heated to 60° for an additional 2 hr. The mixture was poured over ice and diluted to approximately 200 ml. An aqueous solution of 2·5 g of $CuSO_4{\cdot}5H_2O$ was added and the solution neutralised with 20% sodium hydroxide solution until the formation of the olive copper chelate began. The pH of the solution was then adjusted to 9 by the addition of dilute ammonia solution. Warming the solution on a steam bath for 1 hr coagulated the precipitate, which was filtered and washed with dilute aqueous ammonia and water.

The chelate was dissolved in approximately 250 ml of 2*M* hydrochloric acid and the copper removed by precipitation with hydrogen sulphide. After coagulation of the copper^{II} sulphide by warming the solution, the sulphide was separated by filtration. The filtrate was neutralised with 20% aqueous sodium hydroxide, then saturated with carbon dioxide. After standing several hr, the precipitate was collected, washed with water and dried. The crude product was taken up in methanol and recovered by evaporation or alternatively, by precipitation with ether. The pure hydrated betaines were obtained as small dark red needles after two recrystallisations from 90% ethanol. Upon drying the betaines turned to a dark purple.

The chloride-hydrochloride is obtained by saturation of a methanolic solution of the betaine with hydrogen chloride, precipitation of the salt with a 1:1 acetone-ether mixture, and recrystallisation from 90% ethanol, to which several drops of hydrochloric acid had been added to prevent dissociation.

5-(8-*Hydroxy*-5-*quinolylmethyl*)-8-*hydroxy*-1-*methylquinolinium chloride* (*I in Table I*) (*alternate method*)

A solution of 0·005 mole of 5-hydroxymethyl-8-hydroxy-1-methyl-quinolinium methosulphate (1·5 g) (XIV) and 0·01 mole of 8-quinolinol (1·5 g) in 10 ml of glacial acetic acid was prepared and 6 ml of concentrated sulphuric acid added dropwise. The mixture was allowed to stand at room temperature for 2 days, then heated at 60° for 2 hr. The mixture was poured over ice and neutralised with 20% sodium hydroxide and steam distilled. The pH of the remaining aqueous solution was adjusted to approximately 8·5 and the solution extracted with benzyl or amyl alcohol. An equal volume of ether is added to the combined alcoholic extracts and the resulting solution extracted with 0·1*M* hydrochloric acid. This acidic extract was treated with ether to remove the remaining alcohol and evaporated to yield 0·3 g (15%) of I, melting at 319–322° (dec.).

Determination of Spectra and Ionisation Constants

Ultraviolet and visible spectra were recorded with a Beckman DK-2 Spectrophotometer using 1·004-cm matched silica cells for most measurements and 10-cm cells for very dilute solutions. Visible spectra as a function of pH for a large number of equimolar solutions of I were recorded in order to calculate the ionisation constants by standard procedures.[7]

Distribution coefficients for I between an aqueous buffer and chloroform or benzyl alcohol were estimated by recording the spectrum of the buffered solution (pH 8) before and after extraction of a known volume of solution with a known volume of the solvent. The ratio of absorbance at a given wavelength is the fraction of reagent remaining in the aqueous phase. These measurements were only approximate, but indicated coefficients of 2 and 46 for I extracted into chloroform and benzyl alcohol, respectively.

Infrared spectra were recorded on potassium bromide pellets using a Baird AB-2 spectrophotometer. Spectra of I-IV were very similar, showing broad absorption in the 3-μ region for the bonded hydroxyl as well as broad absorption from about 3·2 to 5 μ indicative of quaternary nitrogen. The presence of the methyl group on the carbon adjacent to methylated nitrogen in II and IV apparently gave a double maximum at 6·17 and 6·23 μ, while the other two compounds (I and III) had only a single peak at 6·20 μ. Other bands were not assigned.

Formation of Chelates

Qualitative tests at pH 5 and 9 were run in accordance with previous procedures.[2] Results are described before *Experimental*.

A number of chelates of I with metals were precipitated at pH 9, filtered, washed, dried and weighed. Analysis of these for metal content by ashing to the corresponding metal oxide gave the following results:

Cu^{II}—Calcd. for $Cu(C_{20}H_{15}N_2O_2)_2 \cdot 2H_2O$: Cu, 8·7; found: Cu, 8·7.
Fe^{III}—Calcd. for $Fe(C_{20}H_{15}N_2O_2)_3$: Fe, 5·6; found: Fe, 5·7.
Zn^{II}—Calcd. for $Zn(C_{20}H_{15}N_2O_2)_2$: Zn, 9·4; found: Zn, 9·4.
Al^{III}—Calcd. for $Al(C_{20}H_{15}N_2O_2)_3$: Al, 2·8; found: Al, 3·1.

Acknowledgement—This work was supported by a National Science Foundation Grant.

Zusammenfassung—Die in der Überschrift genannten Verbindungen sowie verwandte Substanzen wurden dargestellt, charakterisiert und als solvatochrome chelatbildende Reagentien geprüft. Diese Reagentien zeigen große Farbänderungen je nach Lösungsmittel und die Chelate sind ebenfalls solvatochrom, obwohl sie in den meisten gebräuchlichen Lösungsmitteln unlöslich sind. Reagentien mit einer 2-Methylgruppe neben dem chelatbildenden Zentrum fällen kein Aluminium; dieser Effekt kann als Farbreaktion auf Aluminium verwendet werden.

Résumé—On a préparé, caractérisé, et essayé les composés du titre et des substances apparentées comme agents chélatants donnant des solvats colorés. Ces réactifs présentent d'importantes variations de couleur en fonction du solvant, et les chélates, quoique insolubles dans les solvants les plus usuels, sont également "solvatochromes." Les réactifs qui ont un groupement 2-méthyl adjacent au centre chélatant ne précipitent pas l'aluminium, et ce fait peut être mis à profit pour un essai coloré de l'aluminium.

REFERENCES

[1] A. Mueller, J. T. Leach and J. P. Phillips, *Talanta*, 1963, **10**, 1087.
[2] J. P. Phillips, J. F. Deye and J. T. Leach, *Analyt. Chim. Acta*, 1960, **23**, 131.
[3] J. P. Phillips and J. T. Leach, *ibid.*, 1962, **26**, 572; H. Fiedler, *J. prakt. Chem.*, 1961, **13**, 77.
[4] J. H. Burckhalter and R. Lieb, *J. Org. Chem.*, 1961, **26**, 4078.
[5] H. Fiedler, *Arch. Pharm.*, 1960, **293**, 609.
[6] H. Vogt, *ibid.*, 1944, **282**, 27.
[7] L. B. Magnusson, C. Postmus, Jr. and C. A. Craig, *J. Amer. Chem. Soc.*, 1963, **85**, 1711.

Talanta, 1964, Vol. 11, pp. 647 to 664. Pergamon Press Ltd. Printed in Northern Ireland

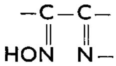
SHORT COMMUNICATIONS

Bisbiacetylmonoxime-ethylenedi-imine and bisbiacetylmonoxime-*o*-phenylenedi-imine as new gravimetric reagents for nickel and palladium

(*Received* 14 *March* 1963. *Accepted* 19 *November* 1963)

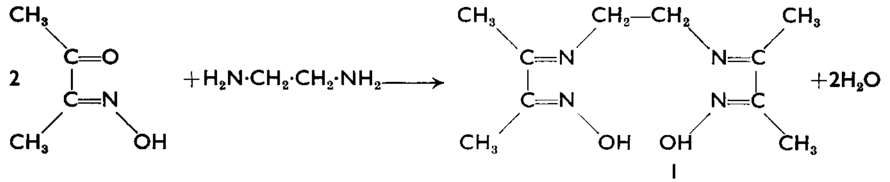
VICINAL diketone dioximes are among the most important organic reagents used in inorganic analysis. Dimethylglyoxime was the first dioxime to be used, as a reagent for nickel and palladium by Tschugaeff,[1] and since then a large number of dioximes have been prepared and tested as analytical reagents.[2–7]

It has been well established that the tautomeric form of the oximes (nitrone form) is responsible for the formation of metal complexes[8] and that the metal involved forms four nitrogen-metal bonds in the dioxime complex. Pfeiffer[8] has shown that if one of the oxime groups is replaced by the imino or methyl-imino group, complex formation occurs in the same fashion. Certain other reagents giving rise to a five-membered chelate ring with the nickel ion and having two co-ordinating nitrogen atoms have a highly selective action towards nickel, the group responsible for the formation of such complexes being

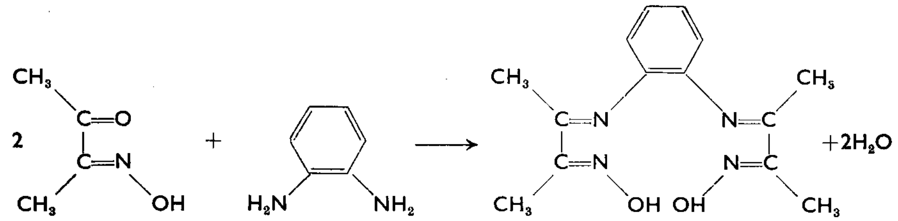


$$\begin{array}{cc} -\mathrm{C}- & \mathrm{C}- \\ \| & \| \\ \mathrm{HON} & \mathrm{N}- \end{array}$$

A possibility exists of condensing diketone monoximes, such as biacetylmonoxime, with certain diamines, such as ethylenediamine and *o*-phenylenediamine, giving rise to the corresponding di-imines. These compounds should have two salt-forming and two co-ordinating nitrogen atoms and give rise to tetradentate ligands.



I



II

The above possibility has now been verified experimentally and the new reagents, bisbiacetylmonoxime-ethylenedi-imine(I) and bisbiacetylmonoxime-*o*-phenylenedi-imine(II), form precipitates with nickel and palladium ions in which the metal and the reagent are present in the ratio of 1:1. As with other dioximes, such precipitates can be used for the gravimetric determination of these metal ions.

EXPERIMENTAL

Synthesis of the reagents

Ten g of biacetylmonoxime[9] were dissolved in 100 ml of water, 3·5 g of ethylenediamine or 5 g of *o*-phenylenediamine were added and the mixture was refluxed for about 1 hr. On cooling in ice, colourless crystals separated in the former case and pale yellow crystals in the latter case. Both compounds were recrystallised from ethanol:—

Compound I: m.p. 242° (with decomposition); 23·8% of N found, $C_{10}H_{18}O_2N_4$ requires 24·8% of N.

Compound II: m.p. 179°; 20·0% of N found, $C_{14}H_{18}O_2N_4$ requires 20·4% of N.

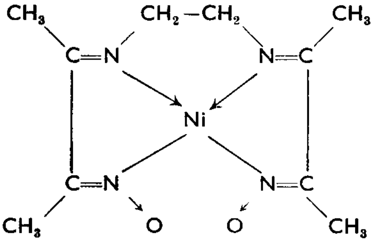
Gravimetric determination of nickel and palladium with the proposed reagents

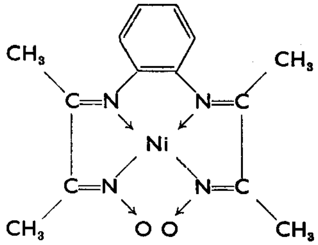
Reagents. One percent solutions of the reagents (I and II) were prepared in aqueous ethanol. A nickel solution was prepared by dissolving 19·735 g of AnalaR ammonium nickel sulphate in 1 litre of water, and a palladium solution by dissolving 1 g of palladium chloride in 500 ml of water. The strengths of the nickel and palladium solutions were checked gravimetrically using dimethylglyoxime.[3]

Procedures. To an aliquot of the nickel solution containing hydrochloric acid an excess of the reagent (I or II) was added, followed by aqueous ammonia till the solution became slightly ammoniacal. The red precipitate of the nickel complex obtained with both reagents was filtered using sintered glass crucibles and dried at 110° for 1 hour.

In the case of palladium a yellow precipitate was formed with both reagents in the presence of hydrochloric acid and it was determined in a similar way to that with the usual dioximes.[3]

By analogy with the dioxime complexes of nickel and palladium, the following structures have been assigned to the complexes with I and II:





Some typical results of determinations with the new reagents are given in Table I. Compound II has a more favourable conversion factor than dimethylglyoxime.

TABLE I

Determination of Nickel

	Ppt., *mg*	Ni, *mg*		Error, %
		Found	Taken	
Compound I	211·7	43·95	43·87	0·18
	175·5	36·43	36·35	0·22
Compound II	177·4	31·49	31·42	0·23
	185·5	32·92	32·90	0·10

Determination of Palladium

	Ppt., *mg*	Pd, *mg*		Error, %
		Found	Taken	
Compound I	205·8	76·26	76·18	0·10
	185·9	59·99	60·12	0·21
Compound II	223·0	62·84	62·95	0·18
	212·5	59·87	59·75	0·20

TABLE II

Metal ion	Mole ratio of Ni:other metal	Masking agent	Remarks
Fe^{II}	1:1	Acetate	Any Fe^{III} first reduced
Fe^{III}	1:1	Tartrate	Any Fe^{II} first oxidised
Co^{II}	1:1	Cyanide	—
Cu^{II}	1:1	Acetate	—
Ca^{II}, Mg^{II}	1:2	—	—
Zn^{II}	1:2	Acetate	—
Bi^{III}	1:0·5	Unsatisfactory	Prior separation necessary

Effect of foreign ions. Although the proposed reagents are highly selective for nickel, some metals interfere in its quantitative determination. These should either be removed by a prior separation or masked by suitable agents (see Table II). Because the precipitation of palladium takes place in an acidic medium, most of the common metals do not interfere.

N. K. MATHUR
C. K. NARANG

Department of Chemistry
M.B.M. Engineering College
University of Jodhpur
Jodhpur, India

Summary—The condensation products of diketone monoximes with diamines have been shown to form precipitates with nickel which contain metal and reagent in the ratio 1:1, and can be used for the gravimetric determination of nickel.

Zusammenfassussung—Es ist gezeignet worden, dass die aus Diketonmonoximen und Diaminen entstehenden Kondensationsprodukte mit Nickel Niederschläge bilden, welche Metall und Reagens in Verhältnis 1:1 enthalten. Diese können zur gravimetrische Nickelbestimmung dienen.

Résumé—Les monoximes de dicétones réagissent avec les diamines en produisant des composées qui donnent avec le nickel des complexes dont la composition metal: nickel égal est à 1:1. Ces complexes peuvent être utilisées pour le dosage du nickel.

REFERENCES

[1] L. Tschugaeff, *Z. anorg. Chem.*, 1905, **46**, 144.
[2] H. Diehl, *The Applications of the Dioximes to Analytical Chemistry.* G. Frederick Smith Chemical Co., Columbus, Ohio, 1940.
[3] W. Vander Haar, R. C. Voter and C. V. Banks, *J. Org. Chem.*, 1949, **14**, 836.
[4] C. V. Banks, D. T. Hooker and J. J. Richard, *ibid.*, 1956, **21**, 547.
[5] W. J. Frierson and N. Marable, *Analyt. Chem.*, 1962, **34**, 210.
[6] J. S. Dave and A. M. Talati, *J. Indian Chem. Soc.*, 1960, **37**, 578.
[7] G. B. Bachman and D. E. Welton, *J. Org. Chem.*, 1947, **12**, 221.
[8] P. Pfeiffer and J. Richarz, *Ber.*, 1927, **61B**, 103;
P. Pfeiffer, J. Richarz, H. Buchholz and O. Angern, *Ber.*, 1930, **63B**, 1811.
[9] W. L. Semon and V. R. Damerell, *Organic Syntheses, Collective Vol. II.* J. Wiley and Sons, New York, 1943, p. 204.

Amperometric determination of lanthanum as molybdate

(*Received* 19 *April* 1963. *Accepted* 25 *November* 1963)

IN an earlier publication[1] the authors studied the reaction of lanthanum nitrate with sodium molybdate and some of its analytical applications by e.m.f. measurements. The present investigation was undertaken with a view to substantiating the earlier results and to studying the possibility of developing the reaction as an analytical method for the determination of lanthanum.

EXPERIMENTAL

Reagents

Merck's guaranteed extra pure lanthanum nitrate and sodium molybdate were used and their solutions prepared in air-free conductivity water. The lanthanum solution was standardised potentiometrically as oxalate[2] and the molybdate solution as the 8-hydroxyquinoline complex.[3] The pH of the lanthanum and molybdate solutions, measured by means of a glass electrode, was 5·3 and 7·4, respectively.

Apparatus

A manual polarograph with scalamp galvanometer as a current recorder was used for the amperometric titrations; the dropping mercury cathode was used in conjunction with a saturated calomel electrode connected to the electrolysis cell by a low resistance salt bridge. The drop time in general was 3–3·5 sec. Both direct and reverse amperometric titrations were carried out at an applied potential of $-1·5$ V (*vs.* S.C.E.). At this potential the lanthanum ion yields a diffusion current proportional to its concentration, while the molybdate ion does not produce any wave in neutral or alkaline medium except the residual current of the sodium ion. Twenty ml of either lanthanum or molybdate solution containing 0·01% of gelatine were taken in the electrolysis cell and the dissolved oxygen removed by bubbling nitrogen through the solution for 10–15 min. After each addition of the titrant, the galvanometer deflection was read and the corresponding current calculated (corrected for the dilution effect[4]), then plotted against the volume of titrant added (Figs. 1 and 2). The titrations were also performed in the presence of ethanol. The presence of an indifferent electrolyte was not found necessary because the sodium nitrate formed during the reaction was quite sufficient to eliminate the effect of migration current. The end-point was obtained graphically making allowance for the volume change during the titration. The results are recorded in Table I.

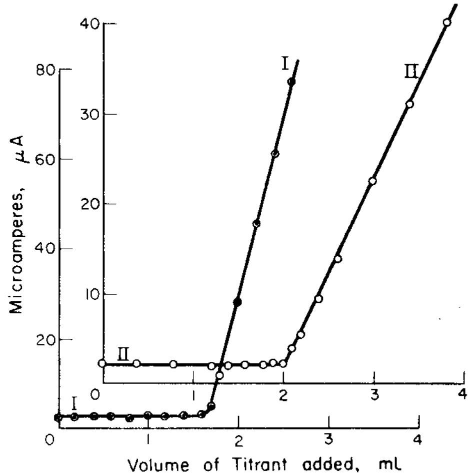


FIG. 1.—Direct amperometric titrations at an applied potential of $-1·5$ V (*vs.* S.C.E.):
I—$0·1000M$ $La(NO_3)_3$ added to 20·0 ml of $0·0125M$ Na_2MoO_4,
II—$0·0333M$ $La(NO_3)_3$ added to 20·0 ml of $0·0050M$ Na_2MoO_4.

TABLE I.—AMPEROMETRIC DETERMINATION OF LANTHANUM BY DIRECT AND REVERSE METHODS AT AN APPLIED POTENTIAL OF $-1·5$ V (*vs.* S.C.E.)

Direct titration			Reverse titration		
Lanthanum			Lanthanum		
Present, *g/litre*	Found, *g/litre*	Error, %	Present, *g/litre*	Found, *g/litre*	Error, %
13·900	13·900	0	0·695	0·695	0
4·633	4·5766	1·22	0·278	0·2795	0·54
3·089	3·0482	1·33	0·1853	0·1824	1·56

DISCUSSION

Figs. 1 and 2 represent direct and reverse amperometric titrations between lanthanum nitrate and sodium molybdate in an aqueous medium in the absence of any supporting electrolyte. In the direct titrations (Fig. 1) when lanthanum nitrate is the 'titrant,' at an applied potential of $-1·5$ V molybdate ions do not produce any measurable diffusion current and hence no change in the value of current is observed on the addition of the lanthanum salt till the stoichiometric end-point, where a molecular ratio for $La^{3+}:MoO_4^{2-}$ of 2:3 is reached, after which the diffusion current from the lanthanum ions increases with the addition of the latter.

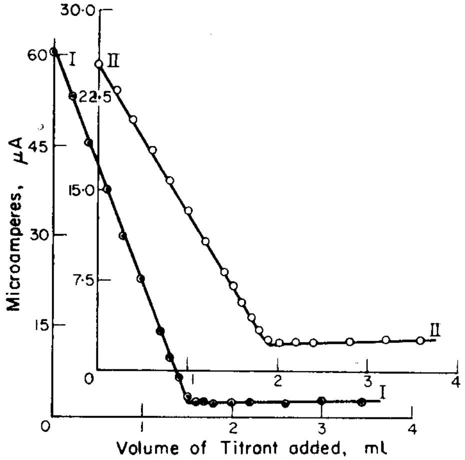


FIG. 2.—Reverse amperometric titrations at an applied potential of $-1·5$ V (*vs.* S.C.E.):
I—0·1000*M* Na_2MoO_4 added to 20·0 ml of 0·0050*M* $La(NO_3)_3$,
II—0·0333*M* Na_2MoO_4 added to 20·0 ml of 0·0020*M* $La(NO_3)_3$.

In the reverse titrations (Fig. 2), addition of the molybdate solution causes a decrease in diffusion current which is proportional to the decrease in the concentration of lanthanum ions. Beyond the end-point when the lanthanum ion concentration becomes zero, the current almost remains constant. The amperometric titration curves indicate a sharp break at the point where the molecular ratio of $La^{3+}:MoO_4^{2-}$ is 2:3, corresponding to the formation and precipitation of normal lanthanum molybdate, $La_2O_3·3MoO_3$, at pH 5–6 (this pH results from the reactants themselves—see *Experimental*). The accuracy and reproducibility of the titrations has been found to be excellent, even at low concentrations of lanthanum salt ($1 \times 10^{-3}M$). The presence of ethanol improves the end-point slightly because it reduces the solubility of the precipitated compound.

The quantitative precipitation of lanthanum as molybdate at pH 5–6 can be used for the amperometric determination of this metal at an applied potential of $-1·5$ V (*vs.* S.C.E.). The method is simple, rapid, accurate and permits the determination of small quantities of lanthanum. Cations which form precipitates with alkali molybdate, *e.g.*, silver, cadmium, cerium^{III}, thorium^{IV}, mercury^{I} and mercury^{II}, and anions which react with lanthanum, *e.g.*, vanadate, tungstate and chromate, interfere and must be absent. The formation of normal lanthanum molybdate as obtained from electrometric results[1] has now been confirmed by amperometric titrations.

Chemical Laboratories
Government College
Kota, Rajasthan, India

R. S. SAXENA
M. L. MITTAL

Summary—The reaction between lanthanum and molybdate ions has been followed by means of direct and reverse amperometric titration in aqueous and aqueous-alcoholic media at an applied potential of $-1·5$ V (*vs.* S.C.E.). The amperometric end-point obtained from the sharp break in the titration curves occurs when the molecular ratio of $La^{3+}:MoO_4^{2-}$ is 2:3 and corresponds to the formation and precipitation of normal lanthanum molybdate, $La_2O_3.3MoO_3$, at pH 5–6. Amperometric titrations yield very accurate and reproducible results and offer a simple and rapid method for the determination of lanthanum as molybdate even at low concentrations ($1 \times 10^{-3}M$ lanthanum nitrate).

Zusammenfassung—Die Reaktion zwischen Lanthan und Molybdat wurde mittels direkter und umgekehrter amperometrischer Titration in wäßrigen und wäßrig-alkoholischen Medien verfolgt. Ein Potential von −1,5 V gegen die gesättigte Kalomelelektrode wurde angelegt. Der als scharfer Knick in der Titrationskurve sichtbare amperometrische Endpunkt liegt beim Molverhältnis $La^{3+}:MoO_4^{2-} = 2:3$, entsprechend der Bildung und Ausfällung von normalem Lanthanmolybdat $La_2O_3.3MoO_3$ bei pH 5–6. Die apperometrische Titration liefert sehr genaue und reproduzierbare Ergebnisse und bietet eine einfache und schnelle Methode zur Bestimmung von Lanthan als Molybdat selbst bei niedrigen Konzentrationen ($1 \cdot 10^{-3}$ M Lanthannitrat).

Résumé—On a suivi la réaction entre les ions lanthane et molybdate au moyen de dosages ampérométriques direct et inverse en milieux aqueux et hydroalcoolique, à u potentiel appliqué de −1.5 V (par rapport à une électrode de référence). Le point équivalent ampérométrique, obtenu à partir de la brisure nette des courbes de dosage, apparaît lorsque le rapport moléculaire $La^{3+}:MoO_4^{2-}$ est 2:3 et correspond à la formation et à la précipitation du molybdate de lanthane normal, La_2O_3, $3MoO_3$, à pH 5–6. Les titrages ampérométriques donnent des résultats très précis et reproductibles et offrent une méthode simple et rapide de dosage du lanthane à l'état de molybdate, même à de faibles concentrations (1×10^{-3} M de nitrate de lanthane).

REFERENCES

[1] R. S. Saxena and M. L. Mittal, *Acta Chim. Acad. Sci. Hung.*, 1962, **34**, 193.
[2] I. A. Atanasiu, *Z. analyt. Chem.*, 1938, **112**, 19.
[3] R. Niericker and W. D. Treadwell, *Helv. Chim. Acta*, 1946, **29**, 1472.
[4] I. M. Kolthoff and J. J. Lingane, *Polarography*. Interscience, New York, 2nd Ed., 1952, p. 890.

Phase titrations—IV:* New applications including the assay of water in pyridine

(*Received* 7 *May* 1963. *Accepted* 19 *June* 1963)

Recently Barreto and Barreto have described a convenient spectrophotometric method for the assay of water in organic solvents.[1] It is based on the development of a purple colour when an organic solvent containing a small amount of water is added to a solution of chloranilic acid in absolute ethanol.

The authors point out that the new method cannot be used for the assay of water in nitrogen-containing solvents, such as pyridine, because they react with chloranilic acid. We therefore suggest the use of phase titrations to supplement the chloranilic acid method, because these are applicable to problems to which the latter method is not. The assay of water in pyridine is given below as an example of the application of phase titration to nitrogen-containing solvents.

The theory, optimum titration conditions and pertinent references are given in the previous papers in this series,[2,3]

Results for 18 new binary solutions of organic solvents which have been analysed by phase titration with water are also included.

---

* Part III, *Talanta*, 1964, **11**, 507.

EXPERIMENTAL

Reagents

Reagent-grade *methanol, acetic acid* (96%) and *acetone*, were obtained from E. Merck A.G., Darmstadt. Reagent-grade *dioxan* and 1,2-*dibromoethane* were obtained from Fischer, Fair Lawn, New Jersey, U.S.A. *Bromobenzene* was a Fischer purified laboratory chemical. *Chloroform puriss.*, was obtained from Hoechst, Frankfurt (M.). Chemically pure *pyridine* and *isopropanol* of unspecified grade were obtained from Riedel De Haën A.G., Seelze-Hannover. *Ethanol* (96·6%) was obtained from Tekel Idaresi, Istanbul. *Distilled water* was used throughout.

Procedure

Six known binary solutions of pyridine and water were titrated with chloroform to obtain a calibration curve of the titre as a function of the volume per cent of the water in pyridine. Synthetic unknown solutions were analysed by comparison with it. Details of the procedure are given in the first paper of this series.[3]

RESULTS AND DISCUSSION

Preliminary tests were made on a number of solvents to determine which would be the best titrant. Chloroform was selected and proved to be excellent although benzene, nitrobenzene and dichloroethane were also promising; bromobenzene, carbon tetrachloride, acetophenone and cyclohexane were not.

A typical end-point (20% water–80% pyridine) was investigated with a Zeiss PMQ II spectrophotometer. Plotting absorbancy, *i.e.*, turbidity, as a function of ml of titrant gave the curve shown in Fig. 1. The earliest phase separation is not easy to observe and takes place before the solution becomes definitely turbid. Hence all solutions were titrated beyond the point of first phase separation to a point at which the increase in turbidity is greater and correspondingly more reproducible.

Eighteen samples, containing 10–40% of water in pyridine were titrated with chloroform. The average error was 0·07 absolute %; the maximum error was 0·2 absolute %. The end-point was good to excellent throughout the optimum titration range of 8–45% water in pyridine.

The accuracy is considerably better than with the chloranilic acid method (relative mean deviation 1·5%, maximum deviation 2·5%) but the present method suffers from the drawback that a suitable titrant must be found for each new system. A less suitable titrant would have given a less distinct end-point and a corresponding reduction in accuracy. The criteria for suitable titrants have been discussed.[3]

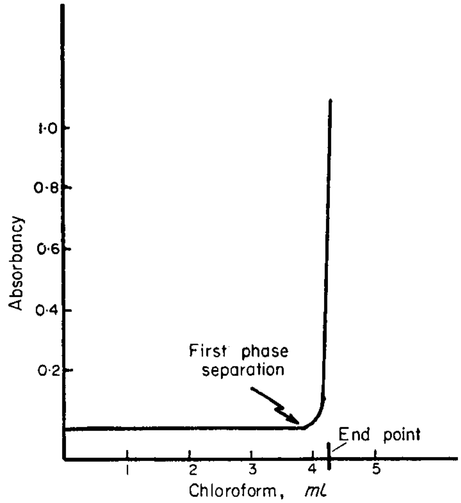


FIG. 1.—Absorbancy at 500 mμ, resulting from turbidity, of a solution of water in pyridine titrated with chloroform.

The assay of water in solvents by phase titration is based on the same principle as the well known cloud-point method.[4,5] In the cloud-point method, a standard amount of an insoluble component is added to a binary mixture of water and some solvent. The temperature at which opalescence appears is then compared with a calibration curve of the temperature of opalescence as a function of composition. We believe that phase titration has the advantage over the cloud-point technique in simplicity and speed because it is easier to carry out a titration than to control and adjust the temperature of a system.

If only a few samples are to be analysed, however, the cloud-point technique has the advantage that the calibration curve need not be made anew, provided that the chemical composition of the insoluble component can be reproduced exactly.[5] Reported results for the cloud-point technique show greater accuracy (0·01–0·02% error) than those for phase titration.

TABLE I.—RESULTS FOR THE TITRATION OF 18 HOMOGENEOUS BINARY SYSTEMS WITH WATER

Sample	Optimum range, %	Number of titrations	Average absolute error, %
Bromobenzene-methanol	2–25	12	0·09
Bromobenzene-ethanol	3–33	12	0·04
Bromobenzene-isopropanol	7–45	12	0·12
Bromobenzene-dioxan	2–20	12	0·07
Bromobenzene-acetone	2–25	12	0·05
Bromobenzene-acetic acid	2–23	10	0·10
Chloroform-methanol	8–60	15	0·13
Chloroform-ethanol	11–50	12	0·12
Chloroform-isopropanol	12–40	12	0·06
Chloroform-dioxan	4–20	9	0·16
Chloroform-acetone	4–30	12	0·09
Chloroform-acetic acid	10–50	11	0·13
1,2-Dibromoethane-methanol	2–25	12	0·06
1,2-Dibromoethane-ethanol	2–20	12	0·07
1,2-Dibromoethane-isopropanol	5–25	12	0·09
1,2-Dibromoethane-dioxan	2–15	12	0·06
1,2-Dibromoethane-acetone	3–20	12	0·04
1,2-Dibromoethane-acetic acid	3–25	12	0·13

The end-point was indicated by the appearance of a distinct permanent turbidity. Titrations and determination of the calibration curve were carried out on the same day.

Table I shows the results for the phase titration of 18 new binary solutions of organic solvents using water as the titrant. The optimum titration range varies slightly with ambient temperature. Binary solutions in which dibromoethane was one component showed good end-points; those with bromobenzene showed excellent end-points; those with chloroform were good in the middle but fair to poor at the extreme ends of the optimum titration range. The end-point appears somewhat more slowly (0·5-min pause) in isopropanol solutions, probably because of the relatively high viscosity of isopropanol.

Acknowledgement—The authors gratefully acknowledge the assistance of the Society of Sigma Xi through a grant in aid of research.

Summary—The assay of water in organic solvents by means of phase titration has been discussed in relation to the chloranilic acid method of Barreto and Barreto (*Analyt. Chim. Acta*, 1962, **26**, 494) and the older cloud-point technique. Results are given for the titration of water-pyridine solutions with chloroform, as representative of the phase titration of a nitrogen-containing compound to which the chloranilic acid method is inapplicable. In addition, results are given for the phase titration of 18 new binary solutions using water as the titrant. They are bromobenzene, chloroform and 1,2-dibromoethane, each in binary solution with methanol, ethanol, isopropanol, dioxan, acetone and acetic acid.

Zusammenfassung—Die Bestimmung von Wasser in organischen Lösungsnitteln durch Phasentitration wird im Vergleich zur Chloranilsäure-methode von Baretto und Baretto und der älteren Trübungsmethode diskutiert. Daten werden angegeben für die Titration von Wasser-Pyridin-Mischungen mit Chloroform als Beispiel für die Phasentitration einer stickstoffhaltigen Verbindung, auf die die Chloranilsäuremethode nicht anwendbar ist. Ferner werden Ergebnisse von Phasentitrationen mit Wasser als Titrant an 18 neuen binären Mischungen angegeben. Es handelt sich um Brombenzol, Chloroform und 1,2-Dibromäthan in Mischungen mit Methanol, Äthanol, Isopropanol, Dioxan, Aceton und Essigsäure.

Résumé—La détermination de l'eau dans les solvants organiques au moyen du dosage de phase a été discutée en relation avec la méthode à l'acide chloranilique de Baretto et Baretto et la méthode ancienne du point de trouble. Les résultats ont été donnés pour des solutions eau-pyridine avec le chloroforme comme exemple de dosage de phase des composés contenant de l'azote, et pour lesquels la méthode à l'acide chloranilique est inaplicable. De plus, les résultats concernant le dosage de phase de 18 nouvelles solutions binaires utilisant l'eau comme agent titrant sont données; ce sont: le bromobenzène, le chloroforme, le dibromo-1,2-éthane en binaire respectivement avec le méthanol, l'éthanol, l'isopropanol, le dioxane, l'acétone et l'acide acétique.

Chemistry Department
Robert Kolej, Bebek
Istanbul, Turkey

D. W. ROGERS*
A. ÖZSOĞOMONYAN

REFERENCES

[1] R. C. R. Barreto and H. S. R. Barreto, *Analyt. Chim. Acta*, 1962, **26**, 494.
[2] D. W. Rogers, *Talanta*, 1962, **9**, 733.
[3] D. W. Rogers and A. Özsoğomonyan, *ibid.*, 1963, **10**, 633.
[4] J. Griswold *et al.*, *Ind. Eng. Chem.*, *Analyt.*, 1946, **18**, 696.
[5] W. Seaman, A. R. Norton and J. J. Hugonet, *ibid.*, 1943, **15**, 322.

A simple method for the determination of carbon in uranium and plutonium carbides

(*Received* 8 *October* 1963. *Accepted* 7 *November* 1963)

INTRODUCTION

ON account of their high thermal conductivity, metal density and melting point, and temperature stability, carbides of uranium and plutonium have been considered as potential fuels for nuclear reactors. It is often necessary to find the carbon content of these carbides; this may be present as both combined carbon and free carbon. The total carbon is determined by combustion at a high temperature in a stream of oxygen, and the carbon dioxide thus evolved is measured either manometrically,[1-3] gravimetrically by absorption in soda asbestos,[4] conductometrically[5,6] or titrimetrically by absorption in standard barium hydroxide solution.[7,8] The free carbon is separated from the sample by dissolving it in hydrochloric acid; the insoluble part, being free carbon, is determined in a similar way.[4,8]

---

* Present address: Chemistry Department, Long Island University, Brooklyn 1, New York, U.S.A.

The present paper describes a simple method in which both combined and free carbon are determined in the same sample by taking advantage of their combustion at different temperatures.

PREPARATION OF THE CARBIDES

Well-powdered mixtures of U_3O_8 and graphite were heated in an atmosphere of argon in a high-current graphite-resistor furnace to 1600° for the formation of mainly uranium monocarbide, and to 2400° for the formation of mainly uranium dicarbide. Carbides of plutonium were likewise prepared by heating, at 2400°, a well-powdered mixture of PuO_2 and graphite. The carbide pellets were powdered in an argon atmosphere, and were stored dry in ground-glass stoppered tubes filled with argon.

THERMOGRAVIMETRIC ANALYSIS

Ten mg of the carbide under investigation were loaded on to the pan of a silica spring thermobalance,[9] and the weight changes in air were observed as a function of temperature; the rate of heating of the furnace being 5°/min. Uranium carbides started to decompose at 250°; for plutonium carbides the temperature was 300° (Fig. 1). The weight of the sample increased, showing the formation of oxide from the carbide. There was no change in weight for either carbide between 500 and 600°, which showed that the carbides are oxidised below 500°. Above 600° there was a loss of weight from the oxidation of free carbon; and at 800° there was complete combustion of carbon, leaving the metal oxides. This behaviour clearly showed the possibility of determining combined carbon in a combustion tube heated at 500°, and free carbon by heating the same sample above 800°, in each case determining the carbon dioxide evolved.

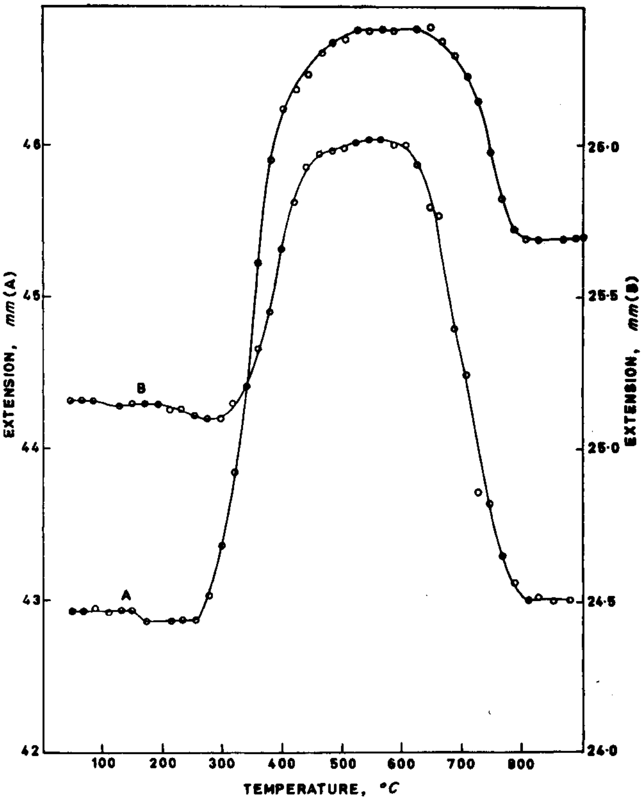


FIG. 1

DETERMINATION OF CARBON

The carbide sample (2–10 mg), weighed in a platinum microcombustion boat, was placed in a quartz combustion tube and heated at 500° for 45 min, passing a current of oxygen, purified by a

U-tube packed with "Carbosorb" (soda asbestos) and Anhydrone, through the combustion tube at the rate of a few bubbles per sec as counted by a sulphuric acid bubbler. The liberated carbon dioxide was absorbed in two conical flasks, each containing 10 ml of $\sim$0·05*N* barium hydroxide solution. The carbon dioxide was determined by titrating the excess barium hydroxide against standard hydrochloric acid solution from an Agla microsyringe, using phenolphthalein as indicator. The same sample was thereafter heated at 900° for 45 min, and the liberated carbon dioxide was again determined. All titrations were performed in a nitrogen atmosphere to prevent absorption of any atmospheric carbon dioxide. The results are given in Tables I and II.

TABLE I.—ANALYSIS OF URANIUM CARBIDES

No.	Wt. of sample, *mg*	Combined carbon* *mg*	Combined carbon* %	Free carbon *mg*	Free carbon %
1.	10·66	0·8868	8·32	0·1128	1·06
2.	15·32	1·2852	8·39	0·1488	0·97
3.	7·13	0·5940	8·33	0·0756	1·06
4.	8·71	0·6948	8·00	0·0864	0·99
5.	7·36	0·6000	8·17	0·0756	1·03
6.	11·93	0·9720	8·15	0·1236	1·04
7.	12·37	1·0200	8·25	0·1260	1·02
8.	12·20	1·0080	8·26	0·1200	0·98
	Average		8·23		1·02
	Standard deviation		1·6%		3·2%

TABLE II.—ANALYSIS OF PLUTONIUM CARBIDES

No.	Wt. of sample, *mg*	Combined carbon* *mg*	Combined carbon* %	Free carbon *mg*	Free carbon %
1.	4·93	0·4464	9·05	0·2376	4·82
2.	3·85	0·3504	9·10	0·2076	5·39
3.	3·59	0·3300	9·19	0·1776	4·95
4.	2·81	0·2580	9·18	0·1500	5·34
5.	2·505	0·2244	8·96	0·1284	5·13
6.	2·595	0·2364	9·11	0·1332	5·13
	Average		9·10		5·13
	Standard deviation		0·3%		3·9%

TABLE III.—URANIUM CARBIDES

Wt. of sample, *mg*	Differential temperature method: Combined carbon*, %	Differential temperature method: Free carbon, %	Conventional method: Free carbon, %
10·230	4·52	9·36	
6·470	4·30	9·16	
5·075	4·47	9·15	
6·395			8·88
7·420			9·12

* Based on the total weight of sample.

COMPARISON WITH CONVENTIONAL METHOD

To test the reliability of this method, samples of uranium and plutonium carbides were analysed by the new and the conventional methods, and the results were compared. In the conventional method, the weighed sample was heated with 5*M* hydrochloric acid for 2 hr to decompose the carbide. The free carbon, which remains unaffected, was centrifuged, washed thoroughly with water, alcohol, acetone and ether to remove the solid and liquid hydrocarbons, and determined as described earlier. The results are given in Tables III and IV.

TABLE IV.—PLUTONIUM CARBIDES

Wt. of sample, *mg*	Differential temperature method		Conventional method
	Combined carbon,* %	Free carbon, %	Free carbon, %
3·200	9·04	8·25	
4·120	8·62	8·27	
3·760	9·00	8·04	
2·25			8·27
2·05			8·20

* Based on the total weight of the sample.

CONCLUSION

The conventional method for the determination of combined carbon and free carbon requires two samples, and the value for combined carbon is obtained by taking the difference between the total carbon present and the free carbon determined separately. The error in this method is, therefore, likely to be greater. In the present method, both combined and free carbon are determined separately in the same sample, thus saving time and reducing the error.

Summary—A simple method for the determination of combined and free carbon in the carbides of uranium and plutonium is based on the examination of the oxidation of carbide and free carbon thermogravimetrically. The combined carbon (carbide) oxidises to carbon dioxide in air below 500° while the free carbon oxidises above 600°. This allows the determination of both combined and free carbon in a single sample, using a furnace tube and a conventional method for carbon dioxide.

Zusammenfassung—Eine einfache Methode zur Bestimmung von gebundenem und freiem Kohlenstoff in den Carbiden von Uran und Plutonium wird beschrieben, die auf der thermogravimetrischen Untersuchung der Oxydation von Carbid und Kohlenstoff beruht. In Carbiden gebundener Kohlenstoff verbrennt an der Luft unter 500°C zu Kohlendioxyd, der freie Kohlenstoff erst über 600°C. Dies erlaubt die Bestimmung von gebundenem und freiem Kohlenstoff in einer Probe in einem Röhrenofen mit einer gebräuchlichen Bestimmungsmethode für Kohlendioxyd.

Résumé—On décrit une méthode simple pour le dosage du carbone combiné et libre dans les carbures d'uranium et de plutonium, basée sur l'observation de l'oxydation du carbure et du carbone libre au moyen de la méthode thermogravimétrique. Le carbone combiné (carbures) est oxydé à l'air en gaz carbonique en dessous de 500°C cependant que le carbone libre s'oxyde au-dessus de 600°C. Ceci rend possible les dosages du carbone combiné et du carbone libre dans un seul échantillon, par l'emploi d'un four tubulaire et d'une méthode usuelle de dosage du gaz carbonique.

H. D. SHARMA
M. S. SUBRAMANIAN

Radiochemistry and Isotope Division
Atomic Energy Establishment Trombay
Bombay, India

REFERENCES

[1] F. L. Bennett, J. H. Harley and R. M. Fowler, *Analyt. Chem.*, 1950, **22**, 445.
[2] Chemical Services Department, Group Report UKAEA Springfields, IGO-AM/S-151, 2nd Edition.
[3] D. Crossley and G. Phillips, AERE, P3790.

[4] J. L. Drummond, B. J. MacDonald, H. M. Ockenden and G. A. Welch, *J. Chem. Soc.*, 1957, 965, 4785.
[5] B. D. Holt, *Analyt. Chem.*, 1955, **27**, 1500.
[6] A. Lassieur, *Compt. rend.*, 1938, **206**, 606.
[7] *Idem, Rev. Met.*, 1941 **38**, 50.
[8] L. P. Pepkowitz and W. D. Moak, *Analyt. Chem.*, 1954, **26**, 1022.
[9] G. S. Rao and M. S. Subramanian, Report AEET/(Radiochem) 20.

Possibility of automation of potentiometric EDTA titrations

(*Received* 23 *October* 1963. *Accepted* 4 *December* 1963)

In many laboratories automatic and semi-automatic apparatus is in use for the simpler types of titration, *e.g.*, of acids, bases and halides. Because there are also many examples of metal titrations which have to be carried out daily, it was considered worthwhile to investigate the possibilities of automation in this field. Very little has been reported on this subject, so far. Haslam *et al.*[1] described an automatic titration of the hardness of water using an amalgamated silver rod as the indicator electrode. Lacy[2] recently published a photometric titration for the semi-automatic determination of hardness in water.

We have investigated the possibility of automation of the complexometric titration of some 20—mostly common—metals for which well-established titration curves were available from earlier work on manual titrations. These examples include direct and back-titrations—the latter with a copper solution as the titrant—in three different pH ranges that are easy to establish. The work is certainly not exhaustive in the sense that many other possibilities undoubtedly exist.

EXPERIMENTAL

Apparatus

Experiments have been carried out with the aid of the well-known Beckman model K titrator, which could be used without modification. An amalgamated gold wire served as indicator electrode, and a saturated potassium chloride calomel electrode as reference. The amalgamated gold wire was prepared by immersing 3 cm of the top part of a pure gold wire (24 carat, length 10 cm, diameter 1·5 mm) for some min in pure mercury. The electrode had to be cleaned frequently with fine emery paper and re-covered. The calomel electrode was connected with the solution by means of a potassium nitrate/agar bridge. pH values were checked by means of a pH meter, but a good grade of pH paper would have been satisfactory in most cases.

The model K titrator is equipped with an "anticipation circuit" which smooths the approach to the end-point of a titration. The number of titration increments is regulated by a dial, the correct setting of which has to be determined for each kind of titration. This is especially important for electrochemical reactions at the mercury electrode which do not proceed instantaneously.[3]

Reagents

The titrants for direct and back-titrations were 0·01*M* standard solutions of EDTA and of copper nitrate, respectively. The buffers were (a) 10 g of sodium hydroxide with 28 ml of glacial acetic acid diluted to 500 ml with water (acetate buffer), and (b) 8 g of ammonium nitrate with 55 ml of 25% aqueous ammonia diluted to 1 litre with water (ammonium buffer). Nitric acid and potassium hydroxide were used to adjust the pH when necessary. A 0·005*M* solution of mercury-EDTA was prepared by mixing a 0·01*M* solution of mercury^{II} nitrate with an equal amount of 0·01*M* EDTA and then adjusting to pH 4. All reagents were analytical grade.

Procedure

Titrations were carried out in 250-ml beakers in which 20 ml of an approximately 0·01*M* metal solution† were diluted with water to 100 ml. Four drops of 0·005*M* mercury-EDTA solution were

† Chlorides and sulphates must be absent because they interfere with potentiometric determinations using the mercury electrode.

added and the pH established at the values given in Table I. For the lower pH range this was effected with nitric acid, for the pH range 4 to 6 with 10 to 15 ml of acetate buffer and for the higher range with 10 to 15 ml of the ammonium buffer. The correct end-point was derived from curves obtained by manual potentiometric titrations using the same electrochemical system; the values are given in Table I. The "anticipation" used is also given in the table. In the case of back-titrations (*B* in Table I), an excess of 0·01*M* EDTA was added to the beaker before titration with copper nitrate solution.

RESULTS AND DISCUSSIONS

Table I contains data on the accuracy of the 18 automatic titrations that were investigated. The standard deviations are calculated from seven-fold titrations in pure single metal-ion solutions. The accuracy has been determined at optimum and carefully controlled pH values.

TABLE I.—ACCURACY OF AUTOMATIC EDTA TITRATIONS WITH THE BECKMAN MODEL K TITRATOR

Metal	Direct (D) or back (B) titration	Setting of end-point, *mV*[a]	Setting of anticipation[b]	Optimum pH value	Standard deviation, *ml*[c]
Bi	D	+360	1·5	1·7	0·01
Fe	D	+360	2·5	1·8	0·05
Hg	D	+385	2·5	1·9	0·03
In	D	+360	2·5	1·5	0·03
Th	D	+340	2·5	1·6	0·06
Cd	D	+210	3·5	4·5	0·01
Cu	D	+220	3·0	4·6	0·04
Pb	D	+230	3·0	4·5	0·02
Zn	D	+220	3·0	4·6	0·03
Al	B	+220	6·0	4·8	0·03
Ni	B	+230	6·0	4·7	0·08
Ba	D	−72	2·0	10·0	0·10
Ca	D	−50	2·0	10·2	0·05
Mg	D	−55	2·0	9·9	0·13
Sr	D	−65	2·0	10·0	0·09
Co	B	−40	3·0	10·2	0·04
Cr	B	−40	3·0	10·0	0·04
Mn	B	−35	3·0	10·1	0·07

[a] *Vs.* saturated potassium chloride calomel electrode.

[b] These figures refer to our instrument. It may be necessary to alter them for other apparatus.

[c] Ml of 0·01*M* titrant, *viz.* EDTA solution for direct and copper nitrate solution for back-titrations, calculated from a seven-fold titration.

Table II compares the accuracies of automatic titrations with those of manual titrations found in earlier work. In the case of zinc there is only a negligible difference in accuracy; for magnesium the difference is a little larger. The automatic procedure might have been expected to be less accurate,

TABLE II

Metal	Standard deviation, *ml*	
	Automatic	Manual
Zn	0·03	0·02
Mg	0·13	0·035

but the difference actually found is surprisingly small and proves the feasibility of the automatic method. Even in the case of magnesium the relative error is less than 1% when 20 to 25 ml are titrated.

In general it can be said—and this is illustrated by the figures in Table 1—that if the titration curve shows a slight jump, the automatic titration is least accurate. Such curves occur, for instance, when the apparent stability of the metal-EDTA complex to be formed is lower than, say 10^9. At the pH applied this is the case for barium ($K^* = 10^7$), magnesium ($K^* = 10^8$) and strontium ($K^* = 10^8$). Also a curve with a flat top part (*e.g.*, that for thorium) is unfavourable for automatic indication of the end-point. Finally, back-titrations will tend to be somewhat less accurate, because two measurements of volume are necessary.

For work of a routine character, *e.g.*, plant control, it is important to know how far variations in the prescribed titration conditions (dial settings, pH, salt concentration) will affect the accuracy. It has been found that the end-point potential must be set precisely because even small deviations may cause the titration result to be very inaccurate. This is caused by the steep fall or rise of the curves in the region of the equivalence point and their sometimes peculiar shape. This effect can, to a certain extent, be compensated by a high "anticipation", but then titrations become very slow. A low setting of the "anticipation" may lead to overshooting of the end-point and it sometimes renders titration impossible because the apparatus does not stop at all.

It is evident that a lower pH value than prescribed will cause errors because this leads to a lowering of the apparent stability of the metal-EDTA complex concerned, which degrades the titration curves. It has been found that for the medium pH range errors will in the majority of cases not exceed ±0·2 ml of titrant when the pH is maintained between 4·0 and 6·0. Especially for the alkaline range, however, large errors must be expected when the pH deviates only a few tenths from the prescribed value.

The quantity of neutral salt in the titration solution was found not to be very critical. A high concentration leads to a slight shift of the titration curves because of a change in activity coefficients. Titration errors were serious only in the case of the poorest curves. In titrating 100 ml of a $0{\cdot}002M$ solution of calcium ions to which 5 g of potassium nitrate had been added the result was 6% low (1·21 ml of $0{\cdot}01M$ EDTA). For many other metals the difference was less than 0·2 ml.

The possibility of applying the automatic technique to samples that contain more than one metal will have to be studied for each individual case. An example is the determination of the hardness of water which essentially is the titration of the sum of calcium and magnesium. In a four-fold automatic titration of the hardness of tap water we found: 15·59, 15·56, 15·68 and 15·52°G.H., respectively. The extreme values differ by only 1%, which is very reasonable.

R. C. Schonebaum
E. Breekland

Koninklijke/Shell-Laboratorium, Amsterdam
Badhuisweg 3, *Amsterdam-N*
Netherlands

Summary—Experiments are described which show that many metals can be determined in a simple way with the aid of the Beckman model K automatic titrator. As regards accuracy, the method is in many cases practically on a par with manual titrations.

Zusammenfassung—Es wird experimentell nachgewiesen, dass sich viele Metalle mit Hilfe eines automatischen Titrationsapparates (Beckmann, Modell K) einfach bestimmen lassen. In vielen Fällen ist die erzielte Genauigkeit der bei manuellen Titrationen erreichten praktisch gleich.

Résumé—Des expériences démontrent que nombre de métaux peuvent être dosés d'une manière simple à l'aide de l'appareil de titration automatique Beckman, modèle K. La précision atteinte est en beaucoup de cas équivalente à celle obtenue dans les titrations manuelles

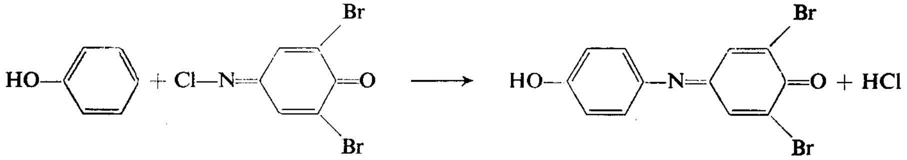
REFERENCES

[1] J. Haslam, D. C. M. Squirrel and I. G. Blackwell, *Analyst*, 1960, **85**, 27.
[2] J. Lacy, *Talanta*, 1963, **10**, 1031.
[3] G. Guérin, J. Desbarres and B. Trémillon, *J. Electroanalyt. Chem.*, 1959/60, **1**, 226.

Zur Kenntnis der Gibbs'schen Farbreaktion auf Phenole

(*Eingegangen am* 13 *November* 1963. *Angenommen am* 18 *November* 1963)

Der von Gibbs[1] entdeckte Nachweis von Phenol mit 2,6-Dibrom-*p*-benzochinon-4-chlorimin beruht auf der Kondensation:



wobei durch gleichzeitige oder nachträgliche Alkalisierung (Natronlauge, Natriumcarbonat, Natriumbicarbonat, Ammoniak, Borax oder Pufferlösungen) ein tiefblaues Produkt entsteht. Gemäß obiger Umsetzung sollte die Farbreaktion mit allen Derivaten des Phenols eintreten, die eine freie *p*-Stellung besitzen. Daß dies jedoch nicht ausnahmslos der Fall ist, hat zuerst Bohdanecký[2] bei der Salicylsäure festgestellt, die nicht reagiert. Da auch bei einigen anderen *o*-substituierten Phenolen mit freier *p*-Stellung die Farbreaktion ausbleibt und somit kein allgemeiner Phenolnachweis möglich ist, mußte die Anwendung des Gibbs'schen Reagens in der Tüpfelanalyse auf bestimmte Fälle beschränkt bleiben. In Betracht kommt der Nachweis von bei Erwärmung flüchtigem Phenol, *o*-Kresol, Thymol, Brenzkatechin, Resorcin und Oxin.[3] Des weiteren ermöglicht der empfindliche Nachweis von Phenoldämpfen den tüpfelanalytischen Nachweis solcher Verbindungen, die bei trockener Erhitzung oder durch den Eintritt in chemische Umsetzungen Phenol abspalten.[4] Schließlich ist noch der Nachweis von Vitamin B_6 (Adermin) mittels des Gibbs'schen Reagens zu erwähnen.[5]

Es wurde festgestellt, daß im Gegensatz zur Salicylsäure das Salicylamid die Gibbs'sche Phenolreaktion zeigt. Dieses verschiedene Verhalten ließ es wünschenswert erscheinen, den Einfluß von *o*- und *m*-ständigen Substituenten auf den Eintritt der Gibbs'schen Phenolreaktion zu ermitteln. Diesbezügliche Versuche wurden mit 2%igen Lösungen hierhergehöriger Verbindungen nach folgenden Arbeitsvorschriften durchgeführt:

Test 1: Auf Filtrierpapier wurde je ein Tropfen der Probelösung, enthaltend 1 mg Probe, und ein Tropfen der benzolischen Lösung von 2,6-Dibrom-*p*-benzochinon-4-chlorimin bzw. des entrsprechenden 2,6-Dichlorderivates so aufgebracht, daß die beiden Tropfen sich auf dem Papier überschneiden. Dann wurde das Papier über Ammoniak geräuchert, wobei bei positiven Ausfall die spindelförmige Überlappung der durch die zwei Tropfen auf dem Filtrierpapier entstandenen Kreise gefärbt wurde. Ein Blindversuch wurde mit dem Reagens und dem Lösungsmittel der Probe angestellt.

Test 2: Wie oben, nur wurde nicht über Ammoniak geräuchert, sondern mit Sodalösung angetüpfelt.

Die Überprüfung von neun *m*-substituierten Phenolen mit freier *p*-Stellung (in Tabelle I) hat

Tabelle I

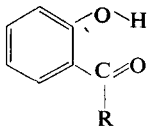
Phenol	Test 1	Test 2
o-Kresol	+ blau	+ blau
m-Kresol	+ blau	+ blau
p-Kresol	keine Rk.	keine Rk.
Salicylaldehyd	+ blau	keine Rk.
m-Hydroxybenzaldehyd	+ blau	+ blau
p-Hydroxybenzaldehyd	keine Rk.	keine Rk.
o-Nitrophenol	keine Rk.	keine Rk.
m-Nitrophenol	+ blau	+ blau[1]
p-Nitrophenol	keine Rk.	keine Rk.
Chromotropsäure	+ blau	+ blau
H-Säure	+ blaugrau	+ blaugrau
K-Säure	+ blaugrün	+ blaugrün
Resorcin	+ violett	+ violett
Orcin	+ braunviolett	+ braunviolett
Naphthoresorcin	+ braunviolett	+ braunviolett

ergeben, daß diese ausnahmslos die Gibbs'sche Farbreaktion zeigen. Abweichungen scheinen demnach lediglich bei *o*-Derivaten zu bestehen, wie folgende Gegenüberstellung in Tabelle II zeigt.

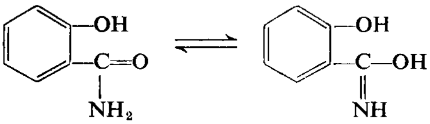
Aus Tabelle I und II geht hervor, daß die Gibbs'sche Farbreaktion bei solchen o-substituierten Phenolen ausbleibt, die im Substituenten ein am C-Atom bzw. N-Atom doppelt gebundenes Sauerstoffatom enthalten. Diese Konstitution ermöglicht eine Chelatisierung des Wasserstoffs der phenolischen Hydroxylgruppe zwischen zwei Sauerstoffatomen, und dies dürfte die Ursache für das Ausbleiben der Reaktion sein, da in diesen Fällen gar keine phenolische Hydroxylgruppe mehr vorliegt:

TABELLE II

Phenole	mit positiver Rk.	mit negativer Rk.
Phenol	blau	Salicylsäure
o-Kresol	blau	Salicylsäuremethylester
Thymol	blau	Salicylsäureisoamylester
o-Phenylphenol	blau	Salicylsäurehydrazid
Brenzkatechin	blau	*o*-Nitrophenol
Guajakol	blau	Salicylaldehyd (mit NH_3 positiv)
o-Aminophenol	blau	Orthovanillin (mit NH_3 positiv)
Glyoxal-bis-(2-hydroxyanil)	blau	
8-Hydroxychinolin	blau	
Salicylaldoxim	blau	
Salicylalhydrazon	grünblau	
Salicylsäureamid	blau	
Orthoeugenol	blau	
Salicylalanilin	blau	



Der Eintritt der Gibbs'schen Farbreaktion bei Salicylamid und Salicylanilid ist offenbar dadurch su erklären, daß in diesen Fällen der Substituent auch in einer tautomeren Imidform vorliegt, die keinen am Kohlenstoff doppelt gebundenen Sauerstoff enthält:



Die Tatsache, daß Salicylsäurehydrazid die Gibbs'sche Reaktion nicht zeigt, deutet darauf hin, daß bei dieser Verbindung eine dem Salicylamid analoge Tautomerie nicht vorliegt, zumindest nicht in dem für die Kondensation erforderlichem Ausmaß.

Daß doppelt gebundener Stickstoff die phenolische OH-Gruppe gegenüber der Gibbs'schen Reaktion nicht maskiert, zeigt die Reaktionsfähigkeit von Salicylaldoxim, Salicylalhydrazon und 8-Hydroxychinolin. Im Einklang damit kann die Reaktionsunfähigkeit von Salicylaldehyd durch Einwirkung von Ammoniakdampf aufgehoben werden, weil hierbei Salicylaldimin entsteht, das kein zur Chelatisierung erforderliches Sauerstoffatom besitzt.

Die Tatsache, daß bei Phenolen mit zur Chelatbildung befähigten Substituenten in *o*-Stellung die Gibbs'sche Farbreaktion ausbleibt, ist zur Charakterisierung von Phenolen von Bedeutung. Der positive Ausfall der Farbreaktion beweist das Vorliegen von Phenolen mit freier *p*-Stellung ohne o-ständige —CHO,COOH oder —COOR Gruppen. Die Anwesenheit solcher Gruppen ist demnach erwiesen, wenn bei positiven Ausfall anderer Nachweisreaktionen auf Phenole mit freier *p*-Stellung die Gibbs'sche Farbreaktion ausbleibt. Von Interesse ist auch die Anwendung der Gibbs'schen

Reaktion zur Unterscheidung von gewissen isomeren Derivaten des Phenols. Von Phenolcarbonsäuren und deren Estern sowie von Hydroxybenzaldehyd gibt es jeweils drei Isomere, von denen lediglich das *m*-Isomere die Gibbs'sche Reaktion zeigt.

Laboratorio da Produçao Mineral
Ministério da Agricultura
Rio de Janeiro, Brazil

F. Feigl

Chemisches Laboratorium
Wien XVIII/110
Teschner 35
Österreich

V. Anger
H. Mittermann

Zusammenfassung—Es wurde der Einfluss von Substituenten auf die Reaktionsfähigkeit von Phenolen gegenüber 2,6-Dibromchinon-4-chlorimin bzw. dessen Chloranalogem untersucht. Es zeigte sich, dass Substituenten in *m*-Stellung wenig Einfluss haben, hingegen in Orthostellung Substituenten mit einer C=O bzw. N=O Gruppe den Eintritt der Reaktion verhindern.

Summary—The influence of substituents on the reactivity of phenols towards 2,6-dibromoquinone-4-chlorimine and its chloro analogue has been investigated. It has been shown that substituents in the *m*-position have little influence, whereas *o*-substituents with a C=O or N=O group prevent the reaction taking place.

Résumé—On a étudie l'influence des substituants sur la réactivité des phénols vis-à-vis de la 2,6-dibromoquinone-4-chlorimine et de son analogue chloré. On a montré que les substituants en méta ont peu d'influence, mais que les substituants en ortho, avec un groupe C = O ou N = O empêchent la réaction.

LITERATUR

[1] H. D. Gibbs, *J. Biol. Chem.*, 1927, **72**, 649.
[2] M. Bohdanecký, *Chem. průmysl*, 1954, **4**, 25; *Analyt. Abs*, 1955, **2**, 2473.
[3] F. Feigl und E. Jungreis, *Analyt. Chem.*, 1959, **31**, 2099.
[4] *Idem, ibid.*, 1959, **31**, 2101; *Talanta*, 1958, **1**, 367.
[5] *Idem, Clin. Chim. Acta*, 1958, **3**, 399.

Talanta, 1964, Vol. 11, pp. 665 to 666. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

Use of "dead-stop" indication of the end-point in chelometric titrations

SIR,

For indicating the end-point of the titration of iron^{III} salt with EDTA, we have used the change of current in a system of two stationary Pt-microelectrodes at a constant applied potential (dead-stop indication).* During the titration of iron^{III} in acidic unbuffered medium at pH 1–1·5, the current changes were found to be maximum 0·1 (μA) at an applied potential of 1–1·4v. The nature of the corresponding titration curves depends on the value of the applied potential, as will be discussed later.

Because indication of the end-point in the titration of iron^{III} with EDTA is possible even in a medium of 0·2*M* HCl, the determination is quite selective. Also, the stabilisation of the current after each addition of the titrant is very rapid, in comparison with the same titration carried out under potentiometric control.[1] This titration with two Pt electrodes can be used for the indirect determination of a series of metals by the back-titration of the excess of EDTA with iron^{III} solution. Preliminary results have shown also the possibility of a direct titration of Cu^{II}, Tl^{III} or U^{IV} with EDTA; and in the presence of small amounts of Fe^{III} with some traces of Fe^{II} it is possible to use dead-stop indication for the direct titrimetric determination of metals forming very stable complexes with EDTA (Th, Zr, *etc.*)

Details of this indication, and methods for the determination of some metals will be published in this Journal at a later date.

F. VYDRA
J. VORLÍČEK

* (NOTE ADDED IN PROOF: The course of this titration can also be followed using dead-stop indication and two graphite electrodes.)

Analytical Laboratory
Polarographic Institute CSAV and
Research Institute of Iron Mines
and Iron Pelleting
Prague, Czechoslovakia

10 *December* 1963

[1] R. Přibil, Z. Koudela and B. Matyska, *Chem. Listy*, 1950, **44**, 222.

Rapid chemical analysis of silicate rocks

SIR:

IN recent years, numerous schemes for the rapid chemical analysis of silicate rocks and minerals have been proposed, and some of these are in widespread use throughout the world.

One of the greatest problems in devising such rapid schemes is that of obtaining a clear homogenous solution of the sample from which aliquot portions may be measured for the various determinations. In particular, the preparation of a solution for the colorimetric determination of silica is somewhat troublesome.

It has been found that a clear aqueous solution of most silicate samples may be quickly and conveniently prepared by the following simple procedure. No element likely to cause serious interference in any of the common determinations is added, and it should be possible to adapt existing methods for use with this method of solution. The procedure is as follows:

Weigh 0·1000 g of the 200-mesh sample into a 55-ml flat-bottom platinum dish, and add 0·50 g of anhydrous lithium metaborate ($LiBO_2$). Mix, and heat over a Meker burner (in an oxidising flame) for 5–10 min.

After fusion is complete, remove the dish from the flame, and drop it (preferably while still red hot) into 125 ml of 2% v/v nitric acid in a 250-ml beaker. Pour 2% nitric acid into the dish until the latter sinks to the bottom of the beaker, and immediately add a Teflon covered stirring bar. Stir at moderate speed (without heating) until solution is complete. This will take about 10 min.

Transfer to a 200-ml flask, dilute to the mark with water and mix. The solution is now ready for use. Aliquot portions may be removed for the determination of silica, alumina, iron, titania, magnesia and the alkaline earths. Because lithium does not interfere seriously with the flame photometry of sodium and potassium, the alkali metals may also be determined.

The solution may also be used for spectrochemical analysis using spark-solution techniques. If this is intended, internal standard may conveniently be added to the dilute nitric acid before the sample fusion.

Lithium metaborate is an extremely active flux, and readily dissolves most of the minor refractory minerals (chromite, ilmenite, *etc.*) commonly found in silicate rocks. The suggested solution procedure is thus not only very much faster than those using hydrofluoric acid, but much more efficient as well. Hydrofluoric acid mixtures do not adequately attack all of the mineral constituents of rocks. The suggestion that the sample be ground to pass a 200-mesh screen is made because of sampling considerations, and not because the fine grinding is necessary for attack by the flux.

Detailed procedures for rapid silicate analysis based on this and other solution methods are at present being developed in this laboratory.

College of Mineral Industries
Pennsylvania State University
118 *Mineral Sciences Building*
University Park, Pennsylvania, U.S.A.

C. O. INGAMELLS

12 *December* 1963

Talanta, 1964, Vol. 11, pp. i to iii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(*Material for this section should be sent directly to the Associate Editor*)

BUNDESREPUBLIK DEUTSCHLAND

1.–2. *April* 1964: *GDCh-Fachgruppe "Kern-, Radio und Strahlenchemie"*: Symposium über *Methoden zur Messung weicher β-Strahler:* Karlsruhe.

CZECHOSLOVAKIA

Tuesday 29 *September–Friday* 2 *October* 1964: **Third National Radiochemical Conference:** *Czechoslovak Chemical Society, Nuclear Chemistry Section:* Scientific House, Liblice by Praha.

The following topics are proposed for the Conference:

1. Separation methods in radiochemistry.
2. Radioisotopes in chemical analysis.
3. Hot atom chemistry.
4. Radioisotopes in chemistry and industrial research.
5. Production of radioisotopes.

Original papers are invited. Two copies of a brief abstract (150 words) with names of authors and their address should be sent, not later than 1 May, 1964, to Jaremír Růžička C. Sc., Faculty of Technical and Nuclear Physics, Praha 1, Břehovà 7. Other correspondence and the full text of papers should be sent to Miroslav Křivànek C. Sc., Institute of Nuclear Research ČSAV, Rež by Praha.

DEUTSCHE DEMEKRATISCHE REPUBLIK

14.–17. *April* 1964: **Moderne elektrochemische Analysenmethoden:** Eisenach (Die Hauptvorträge sind in *Talanta*, 1963, **10,** December, i, schon angedeutet worden).

SWEDEN

Monday–Saturday 14–19 *September* 1964: **Third International Measurement Conference and Sixth International Instruments and Measurements Conference:** The Congress halls at *Felkets Hus*, Stockholm.

Approximately 120 papers have been submitted by scientific and technical societies participating in the organisation of the Conference. Topics of general character will be discussed in the Plenary Sessions and in Sections, whereas new methods for measuring specific physical or chemical quantities are to be handled in the Specialised Sections. New developments in the border fields of measurement and automation will again be discussed in a Section organised jointly with the Technical Committee on Components of the International Federation for Automatic Control. The number of papers has been limited so as to secure time for personal discussions, visits to institutes and plants, excursions, etc.

Correspondence regarding registration, accommodation, *etc.*, should be addressed to RESO Congress Service, Stockholm 1, Sweden. Enquiries regarding the scientific programme should be directed to IMEKO Secretariat, Budapest 5, P.O.B. 3, Hungary. Information regarding the Commercial Exhibition may be obtained from the Exhibition Management, AB Anders Beckman, Birger Jarlsgatan 13, Stockholm C, Sweden.

UNITED KINGDOM

Thursday 2 *April* 1964: Contributions from Research Workers in Universities and Colleges of Advanced Technology: *Society for Analytical Chemistry:* University College, Gower Street, London W.C.1.

Monday–Thursday 6–9 *April* 1964: **Anniversary Meetings:** *Chemical Society:* University, Edgbaston, Birmingham 15.

This will include a Symposium on **New Methods of Organic Analysis** the programme for which is as follows:

Wednesday 8 April, Afternoon	
Qualitative organic analysis.	F. Feigl
Determination of organic functional groups.	F. E. Critchfield
Some instrumental methods in organic anlaysis.	J. R. Majer
Thursday 9 April, Afternoon	
General developments in organic analysis.	R. Belcher
Analysis of organic compounds by titration in non-aqueous media.	E. A. M. F. Dahmen
Organic polarography.	P. Zuman

Further information may be obtained from The Chemical Society, Burlington House, London W.1.

Friday 17 *April* 1964: **Fluorine and Teeth Decay** G. N. JENKINS: **Chemical Additives in Foods** J. MARKLAND: *Society for Analytical Chemistry, North of England Section* and *Scottish Section*: Central Hotel, Victoria Viaduct, Carlisle. 7.15 p.m.

Wednesday 22 *April* 1964: **Analytical Chemistry, Chemical Analysis and the Analyst, R. C.** CHIRNSIDE: *Society for Analytical Chemistry, Midlands Section* and *Royal Institute of Chemistry, Lea Valley Section:* Luton.

Wednesday 29 *April* 1964: Meeting on **Immunological Assay of Hormones: P. G. H.** GELL and A. J. FULTHORPE: *Society for Analytical Chemistry, Biological Methods Group:* Burlington House, London W.1. 7.00 p.m.

Sunday–Saturday 6–12 *September* 1964: **Summer School in Organic Spectroscopy:** *Royal Institute of Chemistry* in collaboration with *Society for Analytical Chemistry:* School of Pharmacy, Brunswick Square, London W.C.1.

The Summer School will provide an organised and concise presentation of infrared and nuclear magnetic resonance spectroscopy in terms of organic structures. Emphasis will be placed on fundamental principles and basic techniques. There will be morning lectures and small seminar discussion groups each afternoon. Laboratory sessions will also be provided.

Further information may be obtained from the Summer School Secretary: Mr. G. D. CHISMAN, Royal Institute of Chemistry, 30 Russell Square, London W.C.1.

At the **Ninth Annual General Meeting** of the *Western Section* of the *Society for Analytical Chemistry* held on *Friday*, 10 *January*, 1964, the following Officers were elected for the forthcoming year:

Chairman: E. A. HONTOIR
Vice-Chairman: L. E. COLES
Secretary/Treasurer: T. G. MORRIS, Brockleigh, Clevedon Avenue, Sully, Glamorgan.

At the **Twenty-Ninth Annual General Meeting** of the *Scottish Section* of the *Society for Analytical Chemistry* held on *Friday*, 24 *January*, 1964, the following Officers were elected for the forthcoming year:

Chairman: R. A. CHALMERS
Vice-Chariman: J. K. MCLELLAN
Secretary/Treasurer: J. W. MURFIN, Boots Pure Drug Co. Ltd., Motherwell Street, Aidrie, Lanarkshire.

UNITED STATES OF AMERICA

Sunday–Friday 5–10 *April* 1964: **147th National Meeting:** *American Chemical Society:* Philadelphia. This includes Symposia on *Chromatography and Electrophoresis* and on *Chemical Analysis through Systems Control.*

Tuesday 7 *April* 1964: **Applications of High Resolution NMR to Determination of Organic Structures** J. L. HOLCOMB: *Society for Applied Spectroscopy, New York Section:* Hotel Manhattan, 8th and 44th Street.

Thursday–Saturday 16–18 *April* 1964: Course on **Evaluation and Interpretation of Physical and Chemical Testing Methods:** *American Society for Quality Control* and *American Chemical Society, Joliet Section:* Kankakee, Ill.

Sunday–Tuesday 19–21 *April* 1964: **Second Annual Oak Ridge Radioisotope Conference:** Gatlinburg, Tenn.

Wednesday–Saturday 22–25 *April* 1964: **Fourth Rare Earth Research Conference:** Camelback Inn, Pheonix, Ariz.

Wednesday–Friday 11–13 *November* 1964: **Sixth Eastern Analytical Symposium:** *Analytical Groups* of *New York and North Jersey Sections* of *American Chemical Society, American Microchemical Society,* and *Baltimore-Washington, Delaware Valley, New England* and *New York Sections* of *Society for Applied Spectroscopy:* Statler-Hilton Hotel, New York.

Following the successful pattern of previous years, the technical programme will consist of selected invited papers on topics of current interest in chemical analysis and closely related fields. Suggestions for programme topics and speakers are invited from all interested persons, These should be submitted to the Programme Chairman: Dr. LEO SAFRANSKI, E. I. du PONT de Nemours and Co., Plastics Department, Experimental Station, Wilmington 98, Delaware.

American Society for Testing and Materials has announced that the following publications in the field of spectroscopy are now available:
First Supplement to the Molecular Formula List of Compounds, Names and References to Published Infrared Spectra: STP 331-A (Price $4.50; $3.15 to ASTM members).
Index of Mass Spectral Data: STP 356 (Price $18.50; $13.00 to ASTM members).
Molecular Formula List of Compound Names and References to Published Ultraviolet and Visible Spectra: STP 357 (Price $6.00; $4.20 to ASTM members).
Serial Number List of Compound Names and References to Published Infrared Spectra: STP 358 (Price $12.00; $8.40 to ASTM members).

Copies may be obtained from ASTM, 1916 Race Street, Philadelphia, Pa.

ERRATUM—Volume 11

***Page* 2, *line* 7:** this should read *Methods have previously been described*.

***Page* 16, *line* 2 *above formula* XIX:** this should read *In order to study the formation of complexes by arsenazo . . . .*

Page 18, *line* 4 *of Synthesis:* this should read *excess of nitrous acid . . .*

Page* 5, *insert after Zusammenfassung

Résumé—L'utilité analytique particulière de l'Arsenazo-III est due à sa capacité de former des complexes spécialement stables avec certains elements. Ceci permet le dosage en milieu acide fort (HCl, 10 M ou SO_4H_2) des éléments penta- ou quadrivalents: Pa, Np^{IV}, Th, Zr, Hf, U^{IV}; la reproductibilité est bonne, la manipulation facile et l'on ne note que de petites interférences dûes aux anions. La grande sensibilité (0,1–0,01 μg/ml, coefficient d'absorption molaire 50–150 × 10^3) est due au grand effet de contraste de la réaction (changement de coloration durose au vert émeraude, déplacement du maximum d'absorption de 125 mμ), nature de spectre, et enfin possibilité d'atteindre des dilutions extremes sans dissociation des complexes.

Page* 41, *insert after Zusammenfassung

Résumé—Les mélanges formés d'orthophosphate, de ses polymères linéaires supérieurs jusqu'au tridécaphosphate compris et trois polymères cycliques ont pu être séparés par chromatographie d'échange ionique. L'un des polymères cycliques (recontré dans les verres de polyphosphate . . . est probablement le pentamétaphosphate. Sa nature cyclique a été démontrée par dosage des groupes terminaux et chromatographie sur papier, mais les tentatives de dénombrement des atomes de phosphore du noyau ont échouées à cause de la très faible quantité de produit disponible. Évidence est presentée a l'appui de la supposition courante que les phosphates linéaires supérieurs sont élués suivant leur degré de polymérisation.

Page* 46, *insert after Zusammenfassung

Résumé—Une méthode pour le dosage des trimétaphosphates en présence d'oligophosphates linéaires supérieurs au trimère est developpée. Il a été démontré que l'ortho-, lt pyro-, at le triphosphate ne sent pas complètement précipitéspar l'ion baryum, tandis que les phosphates oligomères linéaires de type supérieur sont précipités quantitativement. Ces derniers sont isolés des mélanges de phosphates par chromatographie d'échange d'anions, mélangés avec des quantités connues de phosphates cycliques, at précipités par l'ion baryum. Une erreur moyenne de +0,8 et un écart standard de ±3 micromoles de phosphore de l'ion cyclique a été mise en évidence dans les mélanges contenant de 0 à 203 micromoles de phosphore sous forme de trimétaphosphate en présence de 0 à 81 micromoles de phosphare sous forme de polymères linéaires,

***Page* 49, *line* 1:** this should read *using barium diphenylamine . . .*

***Page* 57, *line* 1:** this should read *between ammonium ion and chloramine-T . . .*

Page* 57, *insert after Zusammenfassung

Résumé—La chloramine-T oxyde quantitativement la thiourée en urée et l'ion sulfate en milieu neutre et en milieu basique. L'oxydation est totale en 2 minutes même en présence d'un léger excès d'oxydant. L'uree et l'ion ammonium ne sont pas gênants si l'oxydation est effectuée en milieu alcalin.

Talanta, 1964, Vol. 11, p. iv. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Application of the measurement of thermoelectric tension in chemical analysis—I: Determination of silicon in cast iron: A. Krajina and J. Dolezal. (19 *December* 1963)

Rapid chemical analysis of silicate rocks: C. O. Ingamells. (20 *December* 1963).

The identification of metavanadate anion by infrared spectroscopy: Ileana Lukács, Constanta Strusievici and Erika Hamburg. (1 *January* 1964).

Correction for the separation of hydrogen isotopes during distillation in the determination of tritium: C. J. Riley and H. Brooks. (2 *January* 1964).

A new spot test for titanium with resacetophenone-oxime: S. G. Kadarmandalgi. (2 *January* 1964).

Potentiometric determination of vanadium as silver orthovanadate: Ram Sahai Saxena and Om Prakash Sharma. (2 *January* 1964).

Separation of Eu^{3+} and Am^{3+} by solvent extraction of their metal-chelate complexes: Tatsuya Sekine and David Dyrssen. (6 *January* 1964).

Ammonium hexanitratocerate-(IV) as an oxidising agent—III: Photometric determination of manganese^{II} through oxidation to manganese^{VII}: G. Gopala Rao, K. S. Murty and P. V. Krishna Rao. (6 *January* 1964).

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—IV: Titrimetric determination of uranium^{IV} alone and in mixtures with iron^{II}, manganese^{II}, cerium^{III} or vanadium^{IV}: G. Gopala Rao and P. Kanta Rao. (6 *January* 1964).

Contribution to the basic problems of complexometry—XV: Determination of thorium and scandium in the presence of each other: Rudolf Přibil and Vladimír Veselý. (6 *January* 1964).

Über eine neue Klasse von Adsorptionsfluoreszenzindikatoren: Antoni Basiński and Kazimierz Kiciak. (13 *January* 1964).

The feasibility of fast neutron-activation analysis for copper content determination in low silesian copper deposits: Ludwik Górski, Włodzimierz Kusch and Jolanta Wojtkowska. (13 *January* 1964).

The photosensitivity of 1,10-phenanthroline complexes with tervalent iron: J. Novák and H. Arend. (17 *January* 1964).

Cation-sensitive glass electrodes: Response to alkali metal ions in partially aquated media: G. A. Rechnitz and S. B. Zamochnick. (18 *January* 1964).

Spectrophotometric determination of anthraquinone disulphonic acid sodium salt and its reduced form: J. Dubik and J. Gallus-Olender. (20 *January* 1964).

Separation of certain cations from mixtures of various cations on ion-exchange papers—IV: Arsenic, cobalt, magnesium, manganese, mercury, nickel and vanadium: Joseph Sherma. (27 *January* 1964).

The conductimetric determination of fluorides: A. de Sousa, A. R. Na̋na and G. E. Cameron. (28 *January* 1964).

Determination of cobalt ions by a differential spectrophotometric method: A. Páll, G. Svehla and L. Erdey. (28 *January* 1964).

A new principle of activation-analysis separations—VII: Substoichiometric determination of traces of arsenic: A. Zeman, J. Růžička, J. Starý and E. Klečková. (28 *January* 1964).

A new principle of activation-analysis separations—VIII: Substoichiometric determination of traces of arsenic: J. Růžička, J. Starý and A. Zeman. (28 *January* 1964).

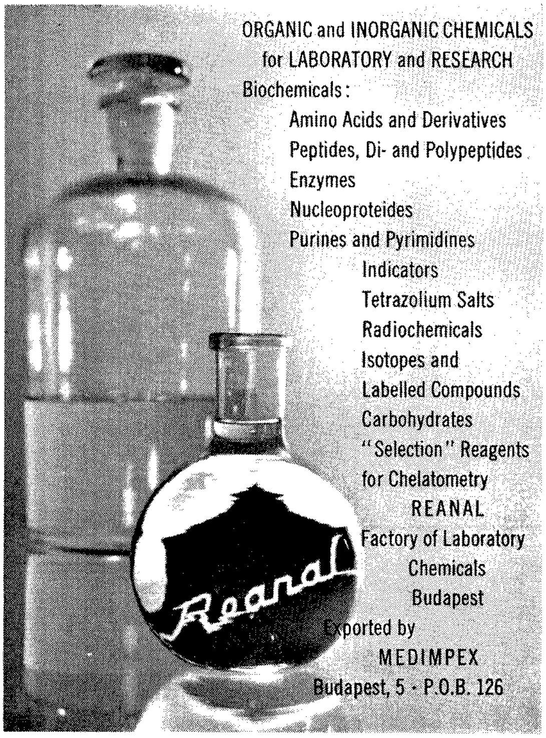
A Technical Writing Service for Industry

Do you need the services of professional technical writers, highly competent illustrators and compilers of modern, effective technical literature? A technical writing service is available to industrial companies and research organizations to prepare, illustrate, print and disseminate instruction manuals, parts lists, user handbooks, sales brochures, internal reports, etc.

The Technical Writing Division is staffed with experienced and highly qualified technical writers, engineers and illustrators and at their disposal are all the very extensive resources and connections of the Pergamon Press.

For further information please write to:

Robert Kiernan,
Pergamon Press Technical Writing Division,
4/5 Fitzroy Square,
London W.1.
Phone: EUSton 4455



ORGANIC and INORGANIC CHEMICALS
for LABORATORY and RESEARCH
Biochemicals:
Amino Acids and Derivatives
Peptides, Di- and Polypeptides
Enzymes
Nucleoproteides
Purines and Pyrimidines
Indicators
Tetrazolium Salts
Radiochemicals
Isotopes and
Labelled Compounds
Carbohydrates
"Selection" Reagents
for Chelatometry
REANAL
Factory of Laboratory
Chemicals
Budapest
Exported by
MEDIMPEX
Budapest, 5 - P.O.B. 126

SPECTROCHIMICA ACTA

Editors: Dr. H. W. Thompson, C.B.E., F.R.S., Dr. V. A. Fassel and Professor M. Kent Wilson

This monthly journal publishes original work dealing with atomic and molecular spectroscopy, with particular reference to problems in chemistry. Emission and absorption spectroscopy over the entire "optical" and X-ray wavelength range and spectroscopy in the microwave region, insofar as it has a direct physiochemical interest, are covered. Papers are on qualitative and quantitative analysis, the determination of molecular structure and of fundamental atomic or molecular data, as well as the design of equipment, description of new experimental methods or the elucidation of general spectral theory.

Write for free inspection copy and subscription rates

PERGAMON PRESS
Headington Hill Hall, Oxford

VOLUME 11, NO. 3 MARCH 1964

CONTENTS

Short communications

Letters to the Editor