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SUMMARIES FOR CARD INDEXES

A current-integrating gamma absorptiometer and data logger for routine uranium analysis: N. P. Wilburn and W. L. Nicholson, *Talanta*, 1965, **12,** 305. (General Electric Company, Hanford Laboratories, Richland, Washington, U.S.A.)

Summary—Uranium concentrations in aqueous and organic solutions are determined by gamma absorptiometry. A ^{241}Am source which emits photons of 60 keV is used with a scintillation detector. The output current from the phototube is integrated for 1 min to give a 2–10 V d.c. signal which is recorded by a data logging system. A unique method requiring aqueous standards only is used to calibrate the system for both aqueous and organic uranium solutions. Detailed statistical analysis of the experimental data is included. A deviation noted from Beer's law is explained by inclusion of scattering effects into the describing model. Solution analyses made using this model result in values accurate to better than $\pm 0{\cdot}5$ g/l. over the range of uranium concentrations from 0 to 120 g/l.

Mutual radiation interference effects of the alkali elements and hydrogen upon the resonance line intensities of the alkali elements in flame spectrophotometry: E. L. Grove, C. W. Scott and Ferris Jones, *Talanta*, 1965, **12,** 327. (School of Chemistry, University of Alabama, Alabama, U.S.A.)

Summary—The mutual interference effects of different concentrations of each of the alkali elements and hydrogen, as the chlorides in solution, on the intensity of the resonance line for four different concentrations of each of the alkali elements have been studied. All concentrations have been expressed in millimoles per litre. The interference effects were greatest on the lowest concentration and least on the greatest concentration of each element. In general, lithium produced the least effect on the other elements, and the other elements had the least effect on lithium. Hydrogen ion, as hydrochloric acid, caused suppression because of the anion effect, with caesium being suppressed the most. Caesium and rubidium caused the greatest enhancement on the other elements. Because of their very low ionisation potentials, the mutual interference effects of rubidium and caesium on each other were found to be very large.

ПОТОК ИНТЕГРИРУЮЩИЙ ГАММА АБСОРПТИОМЕТР И РЕГИСТРАТОР ДЛЯ СЕРИЙНОГО ОПРЕДЕЛЕНИЯ УРАНА:

N. P. WILBURN and W. L. NICHOLSON, *Talanta*, 1965, **12**, 305.

Резюме—Концентрация урана в водных и органических растворах определяется методом поглощения гамма лучей. Применяют источник^{241}Ам который испускает фотоны энергии 60 KeV вместе с сцинтиллационным счётчиком. Выходной ток из фотоэлектрического усилителя интегрируют в течение I мин; получается сигнал постоянного тока 2–10 V который регистрируют в системе даталог. Применяется единственный метод калибровки системы для водных и органических растворов, пользуясь только водными растворами стандартов. Включен подробный статистический анализ экспериментальных данных. Отмеченное отклонение от закона Беера объясняют включением эффектов рассеяния в описанную модель. Точность результатов полученных в анализе растворов пользуясь этой моделью лучше ±0,5 г/л, при концнентрациях урана 0–120 г/л.

ВЗАИМОДЕЙСТВИЕ ИЗЛУЧЕНИЯ ЩЕЛОНЫХ ЭЛЕМЕНТОВ И ВОДОРОДА НА ИНТЕНСИВНОСТЬ РЕЗОНАНСНЫХ ЛИНИЙ ЩЕЛОЧНЫХ ЭЛЕМЕНТОВ В ЭМИССИОННОМ СПЕКТРАЛЬНОМ АНАЛИЗЕ:

E. L. GROVE, C. W. SCOTT and FERRIS JONES, *Talanta*, 1965, **12**, 327.

Резюме—Исследовались эффекты взаимой интерференции различных концентраций всех щелочных злементов и водорода в виде хлоридов в растворе, на интенсивность линий резонанса для четырех различных концентраций каждого из мелочных злементов. Все концентрации выражались в милимолях на литр. Эффекты интерференции были наибольшие при низких концентрациях и наименьшие при высоких концентрациях каждого элемента. Как правило, литий оказывает наименьший эффект на другие элементы, и остальные элементы оказывают наименьший эффект на литий. Водород в виде соляной кислоты, вызывает уменьшение, особенно с цезием, благодаря влиянию аниона. Цезий и рубидий вызывают наибольшее усиление других элементов. Эффекты в заимной интерференции цезия и рубидия очень велики, благодаря их очень низкому ионизационному потенциалу.

Spectrophotometric determination of rhenium(VII) after extraction with 2-thenoyltrifluoracetone: A. K. De and M. S. Rahaman, *Talanta*, 1965, **12**, 343. (Department of Chemistry, Jadavpur University, Calcutta-32, India.)

Summary—A new method is proposed for the determination of rhenium(VII) at the microgram level. 2-Thenoyltrifluoracetone in isoamyl alcohol-benzene extracts rhenium(VII) quantitatively from 7–9*N* sulphuric acid. Treatment of this organic extract with tin(II) chloride and potassium thiocyanate gives a yellow coloured product which can be measured at 430 mμ. Beer's law is valid over the concentration range of 0·5–5 μg of rhenium/ml. The effect of diverse ions has been studied.

Precipitation of zinc sulphide from ammoniacal solutions by thioacetamide: David H. Klein and Ernest H. Swift, *Talanta*, 1965, **12**, 349. (California Institute of Technology, Pasadena, California, U.S.A.)

Summary—The rate at which thioacetamide precipitates zinc sulphide from ammoniacal zinc solutions is controlled mainly by two types of reaction: reactions between the various zinc species and thioacetamide, and reactions between the zinc and the sulphide produced by an ammonia-thioacetamide reaction; the sulphide from the hydroxide catalysed hydrolysis of thioacetamide is relatively small. The rate expression for reactions of the first type is

$$-\frac{d[Zn(II)]}{dt} = \sum_{n=0}^{4} k_n[CH_3CSNH_2][Zn(NH_3)_n{}^{2+}][H^+]^{-2/3}.$$

The rate of precipitation by the second process is controlled by the rate at which sulphide is formed by the ammonia-thioacetamide reaction; this rate expression is

$$-\frac{d[CH_3CSNH_2]}{dt} = -\frac{d[Zn(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2.$$

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ РЕНИЯ(VII) ПОСЛЕ ЭКСТРАКЦИИ С 2-ТЕНОИЛТРИФТОРАЦЕТОНОМ:

A. K. De and M. S. Rahaman, *Talanta*, 1965, **12**, 343.

Резюме—Предлагается новый метод для определения микрограммовых количеств рения. Раствор 2-теноилтрифторацетона в смесе изоамиловый спирт-бензол количественно экстрагирует рений(VII) из 7–9 И серной кислоты. Добавлением хлорида олова(II) и роданида калия к органическому экстракту, получается желтая окраска, поглощение которой можно измерить при 430 ммк. Закон Беера почитается в области 0,5–5 мкг/мл рения. Изучено влияние различных ионов.

ОСАЖДЕНИЕ СУЛЬФИДА ЦИНКА ТИОАЦЕТАМИДОМ ИЗ АММИАЧНЫХ РАСТВОРОВ:

David H. Klein and Ernest H. Swift, *Talanta*, 1965, **12**, 349.

Резюме—Скорость осаждения сульфида цинка тиоацетамидом из аммиачных растворов цинка характеризована двумя родами реакций: реакцией между цинком и тиоацетамидом и реакцией между цинком и сульфидом, образованным реакцией аммиак—тиоацетамид; гидролиз тиоацетамида катализирован гидроокисью дает только незначительные количества сульфида. Скорость реакции первого типа выражена уравнением

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = \sum_{n=0}^{4} k_n[\mathrm{CH_3CSNH_2}][\mathrm{Zn(NH_3)_n}^{2+}][\mathrm{H}^+]^{-2/3}.$$

Скорость реакции другого типа зависима от скорости образования сульфида в реакции аммиак—тиоацетамид; эта скорость выражена уравнением,

$$-\frac{d[\mathrm{CH_3CSNH_2}]}{dt} = -\frac{d[\mathrm{Zn(II)}]}{dt} = k[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2.$$

Precipitation of nickel sulphide from ammoniacal solutions by thioacetamide: David H. Klein, Dennis G. Peters and Ernest H. Swift, *Talanta*, 1965, **12**, 357. (California Institute of Technology, Pasadena, California, U.S.A.)

Summary—The rate of precipitation of nickel sulphide from ammoniacal solutions by thioacetamide is controlled mainly by two types of reaction: reactions between the various nickel species and thioacetamide, and reactions between the nickel species and the sulphide produced by a thioacetamide-ammonia reaction. The sulphide produced by the hydroxide-catalysed hydrolysis of thioacetamide is relatively small. The rate expressions for these two predominant processes are, respectively,

$$-\frac{d[Ni(II)]}{dt} = \sum_{n=0}^{6} k_n[Ni(NH_3)_n{}^{2+}][CH_3CSNH_2][H^+]^{-2/3}$$

and

$$-\frac{d[Ni(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2.$$

Effect of nucleation on rate of precipitation of metal sulphides by thioacetamide: David H. Klein and Ernest H. Swift, *Talanta*, 1965, **12**, 363. (California Institute of Technology, Pasadena, California, U.S.A.)

Summary—Observations have shown that the number of nuclei formed in thioacetamide precipitations of metal sulphides is usually dependent on the first power of the thioacetamide concentration, and is essentially independent of pH, temperature and metal ion concentration. Under certain conditions a second nucleation process has been observed, in which the number of nuclei formed is proportional to the third power of the thioacetamide concentration, and to the inverse first power of the hydrogen ion concentration. The rate of the *direct reaction* between metal ions and thioacetamide is directly proportional to the number of nuclei formed, and the rate expression is otherwise of zero order in thioacetamide. A partial explanation of this effect is proposed.

Selective separation of selenium(IV) by extraction with methyl ethyl ketone: N. Jordanov and L. Futekov, *Talanta*, 1965, **12**, 371. (Institut für allgemeine und anorganische Chemie der Bulgarischen Akademie der Wissenschaften in Sofia und Höheres Pädagogisches Institut in Plovdiv, Bulgaria)

Summary—Selenium(IV) may be extracted by methyl ethyl ketone in a hydrochloric acid medium. The optimum acidity for the extraction has been determined. The kinetics of the association of the selenium chloride complex with methyl ethyl ketone, and of the extraction of the association complex by chloroform, have been examined. In consequence it is possible to separate selenium from considerable amounts of other materials, including tellurium, by extraction. The selenium content of copper concentrates can be determined. A statistical examination of the results, and an estimate of the accuracy of the method are included.

ОСАЖДЕНИЕ СУЛЬФИДА НИКЕЛЯ ТИОАЦЕТАМИДОМ ИЗ АММИАЧНОГО РАСТВОРА:

David H. Klein, Dennis G. Peters and Ernest H. Swift, *Talanta*, 1965, **12**, 357.

Резюме—Скорость осаждения сульфида никеля тиоацетамидом из аммиачного раствора зависима в первой очереди от двух типов реакций: реакции между никелем и ацетамидом и реакции между никелем и сульфидом, образованным реакцией тиоацетамид—аммиак. (Гидролиз тиоацетамида катализирован гидроокисью дает только незначительные количества сульфида). Скорости реакций этих процессов выражены уравнениями:

$$-\frac{d[Ni(II)]}{dt} = \sum_{n=0}^{6} k_n[Ni(NH_3)_n^{2+}][CH_3CSNH_2][H^+]^{-2/3}$$

и

$$-\frac{d[Ni(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2.$$

ЭФФЕКТ НУКЛЕАЦИИ НА СКОРОСТЬ ОСАЖДЕНИЯ МЕТАЛЛИЧЕСКИХ СУЛЬФИДОВ ТИОАЦЕТАМИДОМ:

David H. Klein and Ernest H. Swift, *Talanta*, 1965, **12**, 363.

Резюме—Исследования показали что число центров, образованных при осаждении металлических сульфидов тиоацетамидом зависит от первой степени концентрации тиоацетамида и в сущности не зависит от pH, температуры и концентрации ионов металла. В определенных условиях была наблюдена вторая нуклеация, при которой число образованных центров прямо пропорционально третьей степени концентрации тиоацетамида и обратно пропорционально первой степени концентрации ионов водорода. Скорость "прямой реакции" между ионамы металла и тиоацетамидом прямо пропорциональна числу образованных центров. Попытается объяснить этот эффект.

ИЗБИРАТЕЛЬНОЕ ВЫДЕЛЕНИЕ СЕЛЕНА (IV) ПОМОЩЬЮ ЭКСТРАКЦИИ С МЕТИЛЭТИЛКЕТОНОМ:

N. Jordanov and L. Futekov, *Talanta*, 1965, 12, 371.

Резюме—Селен (IV) хорошо экстрагируется метилэтилкетоном из солянокислой среды. Определена оптимальная кислотность для экстрагирования. Исследована кинетика ассоциации комплекса хлорида селена с метилэтилкетоном и кинетика экстракции ассоциированного комплекса хлороформом. На основе этих данных возможно отделять селен экстрагированием от замечательных количеств других веществ, включая теллур. Этим методом можно пользоваться для определения селена в концентратах меди. Статистически проверены результаты и точность метода.

Amperometry with two polarisable electrodes—III: Chelometric determination of iron(III) using an indication system of two carbon electrodes: J. Vorlíček and F. Vydra, *Talanta*, 1965, **12**, 377. (*Analytical* Laboratory, Polarographic Institute of J. Heyrovský, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—Two carbon (graphite) electrodes have been used for indicating the end-point in the biamperometric titration of iron(III). Satisfactory results are obtained over a wide range of applied potential. The absolute current values are related linearly to the values of the applied potential. At a potential of 0·6–2·0 V the current differences during the titration are from several μA to ten times these values. The influence of pH, applied potential and temperature on the titration have been studied; the effect of interfering elements has been investigated. Under optimal conditions the determination is highly selective and accurate. It is possible to determine 1–150 mg of iron(III).

Contributions to the basic problems of complexometry—XVIII: Masking of iron with fluoride: R. Přibil and V. Veselý, *Talanta*, 1965, **12**, 385. (Laboratory for Analytical Chemistry, Polarographic Institute of J. Heyrovský, Czechoslovak Academy of Sciences, Prague 1, Jilska 16, Czechoslovaka.)

Summary—Very simple conditions have been found for the quantitative precipitation of iron in an acidic medium as K_3FeF_6. This facilitates the complexometric determination of a number of elements, such as copper, lead, nickel, cobalt, zinc and cadmium, in the presence of iron, aluminium, titanium and the rare earths.

Determination of minor and trace elements in nickel by X-ray spectrometry: N. M. Sine and C. L. Lewis, *Talanta*, 1965, **12**, 389. (Falconbridge Nickel Mines Limited, Metallurgical Laboratories, Thornhill, Ontario, Canada.)

Summary—The authors have investigated the applicability of X-ray spectrometry to the analysis of nickel for several elements in the ppm range. Results of the investigation are presented and compared with optical spectrographic analysis as regards sensitivity, precision and accuracy, speed and convenience.

АМПЕРОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ С ДВУМЯ ПОЛЯРИЗИРУЮЩИМИСЯ ЭЛЕКТРОДАМИ—III: КОМПЛЕКСОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЖЕЛЕЗА (III), ПОЛЬЗУЯСЬ ДВУМЯ УГОЛЬНЫМИ ЭЛЕКТРОДАМИ КАК ИНДИКАТОРАМИ:

J. Vorlíček and F. Vydra, *Talanta*, 1965, **12**, 377.

Резюме—Проведено диамперометрическое титрование железа (III) с ЭДТА, пользуясь двумя угольными (графитовыми) электродами как индикаторным прибором. Хорошие результаты получены в широкой области потенциалов. Абсолютная величина тока находится в линейном отношении с примененным потенциалом. При потенциале 0,6–2,0 V ток в течении титрования меняется от несколько МКА до несколько десятин МКА. Исследовано влияние pH, примененного потенциала и температуры на течение титрования и изучено мешание различных элементов. В оптимальных условиях определение обладает хорошой избирательностью и точностью. Можно определить 1–150 мг Fe(III).

ВКЛАДЫ В ОСНОВНЫЕ ПРОБЛЕМЫ КОМПЛЕКСОМЕТРИИ-XVIII: МАСКИРОВАНИЕ-ЖЕЛЕЗА ФТОРИД-ИОНОМ:

R. Přibil and V. Veselý, *Talanta*, 1965, **12**, 385.

Резюме—Разработаны очень простые условия для количественного осаждения железа в форме K_3FeF_6 в кислой среде. Этим способом упрощается комплексометрическое определение ряда элементов как меди, свинца, никеля, кобальта, цинка и кадмия в присутствии железа, аюлминия, титана и редкоземельных элементов, добавлением ЭДТА в избитке и обратным титрованием с раствором соли свинца, пользуясь ксиленолоранжем как индикатором.

ОПРЕДЕЛЕНИЕ В НИКЕЛЕ НЕБОЛЬШОГО КОЛИЧЕСТВА ДРУГИХ ЭЛЕМЕНТОВ И ИХ СЛЕДОВ МЕТОДОМ СПЕКТРОМЕТРИИ РЕНТГЕНОВСКИХ ЛУЧЕЙ:

N. M. Sine and C. L. Lewis, *Talanta*, 1965, **12**, 389.

Резюме—Авторы изучали применимость спектрометрии рентгеновских лучей для определения нескольких элементов в никеле в пределе частей на миллион. Результаты исследования сравниваются с методом оптической спектрографии касательно их чувствительности, точности, скорости и пригодности.

Frontal solubilisation chromatography: Harvey D. Spitz, Herbert L. Rothbart and Wm. Rieman III, *Talanta*, 1965, **12**, 395. (Ralph G. Wright Chemical Laboratory, Rutgers—The State University, New Brunswick, N.J., U.S.A.)

Summary—The behaviour of three non-electrolytes has been studied in both frontal and elution chromatography with an ion-exchange resin as stationary phase and an aqueous solution of ethanol as the mobile phase. On the basis of the plate-equilibrium theory, an equation is derived for the breakthrough graph in frontal chromatography. This is simply the integral of the equation for the graph in elution chromatography. Good agreement is found between the experimental breakthrough results and the equation, as well as between the distribution ratios and plate numbers as evaluated by the two chromatographic methods.

A new principle of activation-analysis separations—IX: Substoichiometric determination of traces of bismuth: Jaromír Růžička, Adolf Zeman and Ivan Obrusník, *Talanta*, 1965, **12**, 401. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Prague 1, Břehová 7, Czechoslovakia.)

Summary—A simple radiochemical separation of bismuth has been developed, based on two dithizone extraction steps, the second of which is a substoichiometric extraction. When copper, gold, mercury, palladium, platinum and silver are not present in interfering amounts, only the substoichiometric dithizone extraction is necessary. The method has been applied to the determination of bismuth by activation analysis in granite and in silicon.

Determination of copper in sea water by atomic absorption spectroscopy: Robert J. Magee and A. K. Matior Rahman, *Talanta*, 1965, **12**, 409. (Department of Chemistry, The Queen's University, Belfast 9, N. Ireland.)

Summary—A commerical atomic absorption spectrophotometer is used without modification to establish the most suitable operating conditions for the determination of copper. Using the direct method of spraying aqueous solutions of copper into the flame, the minimum copper which can be determined is about 25 μg/litre. However, this method is not suitable for determining copper in sea water. A method based on the extraction of the copper-ammonium pyrrolidine dithiocarbamate complex into ethyl acetate and spraying of the organic extract into the flame is satisfactory, and it gives a marked increase in sensitivity.

ХРОМАТОГРАФИЯ МЕТОДОМ ФРОНТАЛЬНОЙ СОЛЮБИЛИЗАЦИИ.

Harvey D. Spitz, Herbert L. Rothbart, and Wm. Rieman III, *Talanta*, 1965, **12**, 395.

Резюме—Исследовано поведение трех неэлектролитов при хроматографии методами фронтального замещения и элюирования, применяя ионообменную смолу как стационарную фазу и водный раствор спирта как подвижную фазу. На основании теории равновесия на тарелках получено уравнение для графического изображения прорыва при фронтальной хроматографии. Это просто интеграл уравнения для графического изображения хроматографии методом элюирования. Найдено хорошое совпадение между экспериментальными данными и уравнением, также и между коэффициентами распределения и числом тарелок, определенными этими двумя хроматографическими методами.

НОВЫЙ ПРИНЦИП ВЫДЕЛЕНИЯ ДЛЯ РАДИОАКТИВАЦИОННОГО АНАЛИЭА—IX: ПОДСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВЫХ КОЛИЧЕСТВ ВИСМУТА:

J. Růžička, A. Zeman and I. Obrusník, *Talanta*, 1965, **12**, 401.

Резюме—Разработано простое радиохимическое выделение висмута, которое основывается на двух экстракциях дитизоном; вторая от этих экстракций подстехиометрическая. Если медь, золото, ртуть, палладий, платина и серебро не присутствуют в мешающих количествах нужно провести только подстехиометрическую экстракцию дитизоном. Метод применен для определения висмута радиоактивационным анализом в граните и в кремние.

ОПРЕДЕЛЕНИЕ МЕДИ В МОРСКОЙ ВОДЕ МЕТОДОМ АТОМНОГО ПОГЛОЩЕНИЯ:

Robert J. Magee and A. K. Matior Rahman, *Talanta*, 1965, **12**, 409.

Резюме—Исследователи пользуются купленным спектрофотометром без модификации чтобы установить оптимальные условия для определения меди. Применяя прямой метод вбрызгивания водных растворов меди в пламя удается определить 25 мкг/л меди. Между тем этот метод не подходящий для определения меди в морской воде. Удовлетворительным оказался метод, который основывается на экстракции комплекса меди с пирролидиндитиокарбаматом аммония в этилацетат и вбрызгиванию органического экстракта в пламя. Кроме того значительно увеличивается чувствительность.

A modification of Leithe's method for determining nitrate: G. W. Latimer, Jr. and O. K. Chambers, *Talanta*, 1965, **12**, 417. (Chemical Division, Pittsburgh Plate Glass Company, P.O. Box 4026, Corpus Christi, Texas, U.S.A.)

Summary—A more stable reagent, $FeSO_4$-HCl, can be effectively substituted for the $FeSO_4$–NaCl–H_2SO_4 reagent originally proposed by Leithe for the determination of nitrate. The NaCl and H_2SO_4 necessary to effect a quantitative reaction are added separately to the sample and blanks, rather than being incorporated in the reagent.

Applications of chelatometry—XVI: Use of copper(II)-EDTA complex for the titrimetric determination of glucose: C. Hennart, *Talanta*, 1965, **12**, 420. (Seraincourt, Seine et Oise, France.)

Summary—Glucose can be determined chelatometrically by measuring the amount of EDTA liberated from its copper(II) complex after reduction of copper(II) to copper(I) oxide. The EDTA is measured, without filtration, by titration with a standard solution of copper(II) sulphate using Murexide as indicator.

ВИДОИЗМЕНЕНИЕ МЕТОДА ЛЕЙТЕ ДЛЯ ОПРЕДЕЛЕНИЯ НИТРАТА:

G. W. Latimer, Jr. and O. K. Chambers, *Talanta*, 1965, **12**, 417.

Резюме—Более постоянный реагент—$FeSO_4$ в соляной кислоте—может успешно заместить реагент $FeSO_4$–$NaCl$–H_2SO_4 первоначално предложен Лейтеом для определения нитрата.

ПРИМЕНЕНИЕ ХЕЛАТОМЕТРИИ—XVI: ПРИМЕНЕНИЕ КОМПЛЕКСА МЕДИ (II) С ЭДТА ДЛЯ ТИТРОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ ГЛЮКОЗЫ:

C. Hennart, *Talanta*, 1965, **12**, 420.

Резюме—Глюкозу можно определить хелатометрически измерением количества ЭДТА, которое освобождается из его комплекса с медью (II) после восстановления окиси меди (II) на окись меди (I). Измеряют ЭДТА без фильтрования, титрованием с стандартным раствором сульфата меди (II) пользуясь мурексидом в качестве индикатора.

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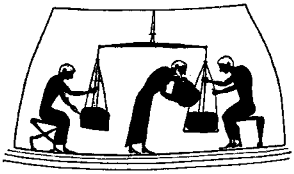

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, Vol. 3. Pergamon Press, London, 2nd Ed., 1956, 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.

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A CURRENT-INTEGRATING GAMMA ABSORPTIOMETER AND DATA LOGGER FOR ROUTINE URANIUM ANALYSIS*

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(*Received* 14 *June* 1963. *Revised* 21 *September* 1964. *Accepted* 20 *November* 1964)

Summary—Uranium concentrations in aqueous and organic solutions are determined by gamma absorptiometry. A ^{241}Am source which emits photons of 60 keV is used with a scintillation detector. The output current from the phototube is integrated for 1 min to give a 2–10 V d.c. signal which is recorded by a data logging system. A unique method requiring aqueous standards only is used to calibrate the system for both aqueous and organic uranium solutions. Detailed statistical analysis of the experimental data is included. A deviation noted from Beer's law is explained by inclusion of scattering effects into the describing model. Solution analyses made using this model result in values accurate to better than ±0·5 g/l. over the range of uranium concentrations from 0 to 120 g/l.

INTRODUCTION

A RECENT study of a solvent extraction process[7] required the analysis of a large number of two-phase samples for uranium concentration in the aqueous and organic phases, aqueous nitric acid concentration and volumetric fraction of organic phase present in a systematic, rapid, relatively foolproof and accurate manner. It is the purpose of this paper to describe the apparatus and procedure used, and the method of calibration.

The techniques involved are standard with the exception of the uranium determinations. Here, gamma absorptiometry is used but the detector current is integrated by an analogue integrator for 1 min rather than making a direct measurement of the steady current. Because the detector current is fluctuating with the source intensity, which has Poisson statistics, the standard deviation of a current measurement varies inversely as the square root of the time over which the measurement is taken. In previously described absorptiometers[3,6] this time would be the time constant of the filtering network for steady currents. When the current is integrated, the measurement time is the integration time. In reference 3 the filter network time constant was 2 sec. Thus, it would be expected that the standard deviation of the current measurements could be reduced by $\sqrt{1/30}$ for this case through a 1-min integration.

EXPERIMENTAL

Apparatus

The uranium concentrations in the aqueous and organic solutions are determined by gamma absorptiometry in a manner similar to that described by Connally[3] and by Whitmer.[6] The solution is placed in a glass cylindrical sample cell which has an inside diameter of 25 mm. Cells of 5-cm (American Instrument Company #5-1000) and 1-cm (American Instrument Company #5-984) path

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* This paper was originally presented to the Instrument Society of America at the Seventeenth International Instrument-Automation Conference and Exhibit at New York City on October 19, 1962.

lengths are used for organic solutions; a different set of 1-cm and 5-cm cells are used for aqueous solutions, and a 5-cm cell containing distilled water is used exclusively as a reference. The measured path length through the solution along the axis of the cell is 5·0000 ± 0·0001 cm for the 5-cm cells and 1·0000 ± 0·0001 cm for the 1-cm cells. The circular faces of the original cells have been ground such that the over-all path length of glass plus solution is equal for all the 5-cm cells and for all the 1-cm cells as determined by optical measurements.

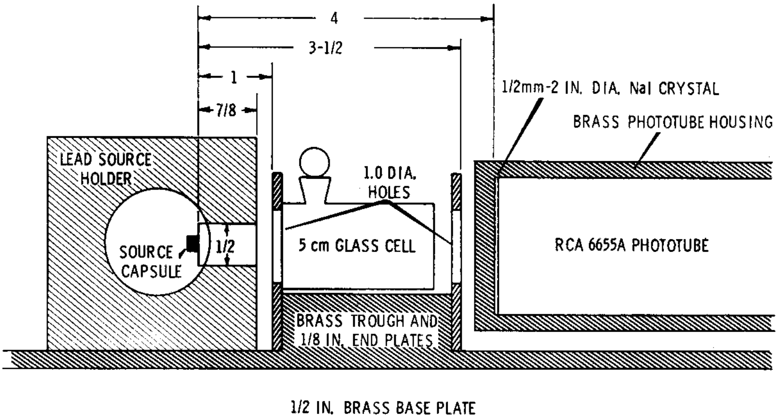

FIG. 1B.—Section drawing of absorptiometer.

The sample cell containing the solution is placed into a trough located between a source housing and a photomultiplier tube-crystal assembly as is pictured in Fig. 1A and shown schematically in Fig. 1B. Ten mg of ^{241}Am (with a half-life of 458 years) is used as a source. The source emits gamma photons of 60-keV energy at a rate of approximately $2{\cdot}8 \times 10^{10}$ gamma photons/min. A gamma energy scan of the source indicates that no significant number of photons of energy greater than 75 keV are emitted. The source is housed in the same manner as described in reference 5. Although the housing itself affords little collimation, the brass plates at the ends of the trough collimate the low energy photons to a beam 1 inch in diameter.

The photons transmitted by the cell and any others which are scattered around the cell are sensed by a scintillation detector consisting of a 2-inch diameter, 0·5-mm thick sodium iodide crystal attached to an RCA type 6655A multiplier phototube all contained in an assembly which has been described.[3] This phototube utilises caesium-antimony dynodes which results in good gain stability; the drift in gain is steady and about 0·6 %/day. The gain of the phototube is temperature dependent (0·3 %/°C). Unless the temperature is cycling up and down 4–5° at a frequency corresponding to that of removal and replacement of the sample cells (as is described later), any temperature and long-term drift effects are eliminated by the data treatment.

A Hammer Electric Company N 401, 500–1800 V power supply, quoted as stable to 1 part in 10^5, is used to provide approximately 1000 V negative to the photomultiplier tube dynode resistor chain, which consists of 100-KΩ wire wound resistors. For this voltage and dynode resistor chain the gain sensitivity to fluctuations is 1 %/V. The high voltage is adjusted periodically so that a 1-μA current is obtained when the reference cell filled with distilled water is in place. The fatigue rate for the RCA 6655A is not detectable for currents up to 1 μA. The high voltage supply is only disconnected from the phototube for maintenance. After reconnection or voltage adjustment, at least 2 days elapse before the system is again used. In this way the phototube "aging" problem is eliminated.

The output current from the phototube is integrated by a Keithley Model 411C picoammeter wired as an analogue integrator by the connection of high quality capacitors (Southern Electronics PC505G4AE) between the input and output leads and the elimination of the feedback resistor. With the 5-cm and 1-cm cells, 5-μF and 10-μF capacitors are used, respectively. The picoammeter as an amplifier has an open loop gain of 2000 stable to within 1 % and the capacitors have temperature coefficients of 0·01 %/°C. Here again, unless either the temperature or amplifier gain is changing in a cyclic manner with a frequency approximating to that of the cell removal and replacement, all effects from drifts cancel in the treatment of the data.

Tests have been run to determine the stability of this integration system and to determine the combined magnitude of system transient effects and hysteresis effects characteristic of the phototube.

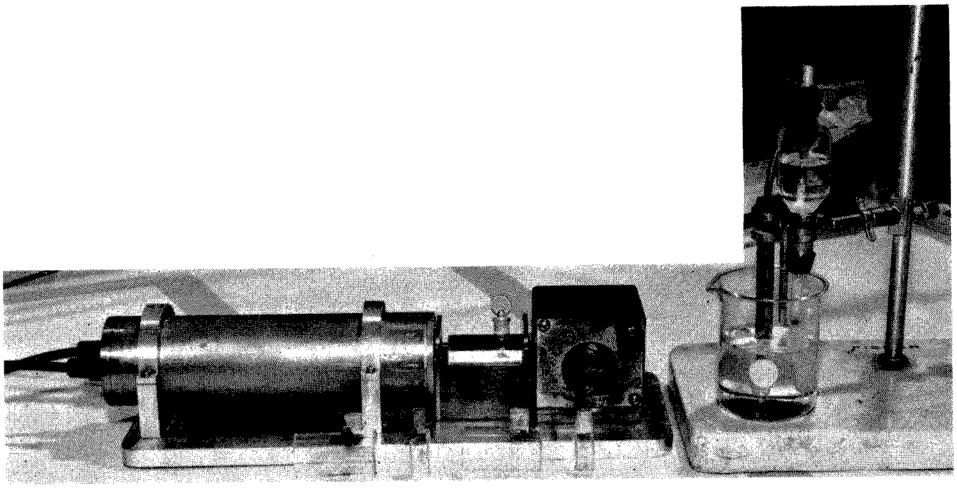

FIG. 1A.—Absorptiometer and pH cell.

These tests, which are described under *Discussion of Errors*, indicate that the integration system is stable to 0·01% and that any such phototube transient effects are less than 0·02%.

An integration is carried out whenever the "SEQUENCE TIMER" cycle is initiated (see Fig. 2). A timer cycle begins upon actuation of one of three pushbuttons mnemonically entitled "REF.", "AQUEOUS" and "ORGANIC". The timer motor drives a cam which in turn actuates three microswitches, labelled "INTEGRATE", "ZERO", "READ PRINT AND STEP" in Fig. 2. The timer cycle consists of the following events:

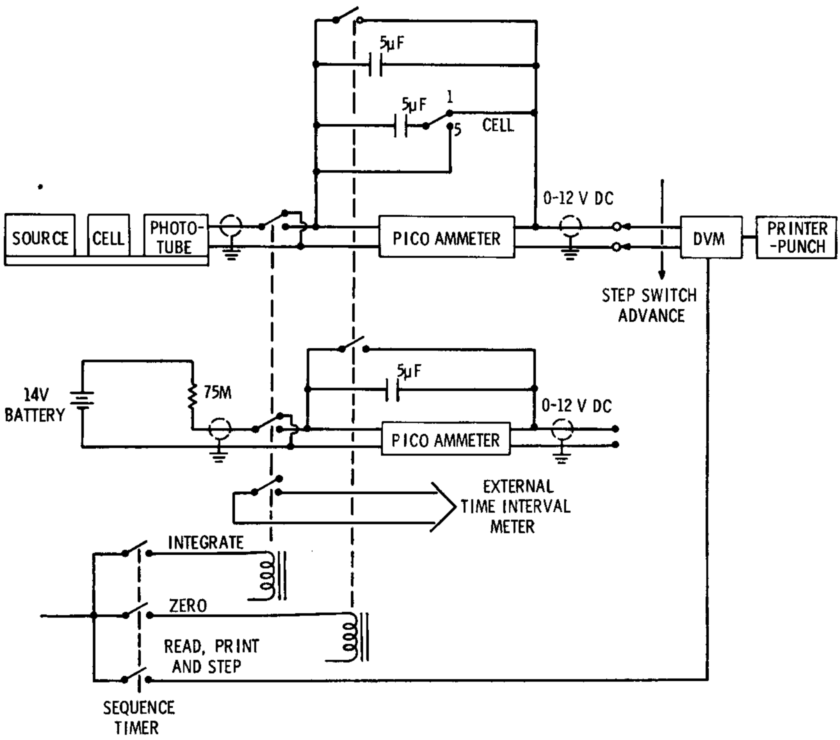

FIG. 2.—Simplified schematic drawing of integrating absorptiometer circuitry.

(1) The "ZERO" switch closes for 1 sec. This causes the integrating capacitors on two parallel integrators to be discharged and hence gives an initial condition of 0 V.

(2) Two sec later the "INTEGRATE" switch closes. This actuates a relay which: (a) connects a relatively constant current source to the lower picoammeter input, (b) connects the phototube anode (which has been grounded until this time) to the upper picoammeter input, and (c) closes a switch which controls an external time interval meter used only during calibrations to give the integration time T. The relative timing errors between these three sets of relay contacts is less than 1 msec.

(3) After approximately 1 min the "INTEGRATE" switch opens, which stops the integrations.

(4) Two sec later the "READ..." switch closes, which allows the digital voltmeter (DVM) to balance. The DVM is a 5-digit Kintel Model 502B, which has an accuracy of 0·01% plus or minus 1 digit and a stability of 0·02% over a period of 1 week.

The DVM balance causes a printout of the output voltage (V_D) from the upper integrator, then a stepping switch advances, and the voltage of the lower integrator (V_S) is read and printed. The latter voltage is proportional to the time elapsed during the integration period, which varies about 0·5% because of timer imperfection. Use of the ratio V_D/V_S in the calibrations eliminates timing and stability errors in the circuitry. Drifts in the 14 V battery-75 M resistor current source are eliminated by the data treatment. This method of controlling and measuring the integration time was selected for its simplicity and low cost.

After all the V_D and V_S are logged for a sample, other voltages obtained from a reference voltage supply (V_{R_0}), two precision potentiometers (V_{R_1} and V_{R_2}) and a pH meter (V_{pH}) are logged in turn. Each voltage is logged into punched paper tape and printed on adding machine tape by a Kintel

Model 467-Tally 420-Hewlett Packard 561A data logging system and has recorded with it a 3-digit identification which contains information as to which type of solution is being analysed (organic, aqueous or reference), which size sample cell was used and from which sample port in the test facility the sample was obtained.

Procedure for a typical sample analysis

The mixed aqueous and organic phases from a sample are first transferred from a 100-ml sample bottle into a clean calibrated 100-ml burette. The phases are allowed to separate and the positions of aqueous-organic and organic-air interfaces are read to the nearest 0·1 ml. These readings are dialed into two appropriately labelled, digital indicating, 10-turn precision voltage-dividing potentiometers which are logged at a later time by the DVM (V_{R_1} and V_{R_2}). The reference cell is then analysed as described above by pressing the "ZERO ANALYSIS" button. An aqueous cell (either 1 or 5 cm depending upon the estimated sample concentration) is filled from the tip of the burette, placed in the trough and analysed by pressing the "AQUEOUS ANALYSIS" button. An additional aqueous sample is withdrawn into a small beaker into which pH electrodes are then immersed (Fig. 1A).

Table I.—Typical data logger output tape

Printer tape	Data logged	
197 − 09387-3[a]	V_P	for first reference analysis (REF_1)
198 − 11252-3	V_S	for first reference analysis (REF_1)
192 − 09542-3[b]	V_P	for aqueous cell analysis (AQ)
193 − 11263-3	V_S	for aqueous cell analysis (AQ)
194 − 08463-3[c]	V_P	for organic cell analysis (ORG)
196 − 11274-3	V_S	for organic cell analysis (ORG)
197 − 09390-3[d]	V_P	for second reference analysis (REF_2)
198 − 11257-3	V_S	for second reference analysis (REF_2)
199 + 14804-3	V_{R_0}	voltage applied across potentiometer
900 + 02041-3	V_{R_1}	aqueous-organic pot reading
901 + 09684-3	V_{R_2}	organic-air pot reading
902 − 00792-3	V_{pH}	pH of aqueous solution reading
↙ Identification ↓ Voltage ↘ Power of 10 by which voltage is multiplied		

[a] First two digits of identification are sample port number.
[b] Third digit of identification is 1 for 1-cm cell, 2 for 5-cm cell.
[c] Third digit of identification is 4 for 1-cm cell, 5 for 5-cm cell.
[d] Third digit of identification is 7 for reference cell.

The electrodes are connected to the pH meter which has a 0–100 mV output amplified in turn by a 30·00 to 1·00 precision d.c. amplifier to give V_{pH}. The remaining aqueous phase in the burette and some organic phase are drained and discarded.

A 1- or 5-cm organic cell is filled from the burette and analysed as described above by pressing the "ORGANIC ANALYSIS" button. Finally, the reference cell is again analysed to complete the sequence. After the V_S is logged for the reference cell, the data logger steps on and successively reads the other voltages as described above. The resulting printed output appears as shown in Table I.

When all samples from a given run have been processed, the punched tape is identified and submitted for data processing. A data reduction code calculates uranium concentrations, *etc.*, as is described in the next section.

With the data-logging and data processing system described in this section, the analyses of 30 two-phase samples can be obtained within 24 hr after they are taken.

Mathematical model of absorption

In the determination of the uranium concentrations from the data voltages the four ratios $(V_P/V_S)_{REF_1}$, $(V_P,V_S)_{AQ}$, $(V_P/V_S)_{ORG}$ and $(V_P/V_S)_{REF_1}$ are first computed. The four analyses in the sequence, reference-aqueous-organic-reference, are uniformly spaced in time; and it is assumed that the reference ratio applicable at the time of the aqueous and organic analyses may be computed from a linear interpolation between the two reference ratios. Two quantities Q are then computed for the aqueous analysis and the organic analysis which are free from drifts inherent in the apparatus—such as battery voltage or resistance change in the circuit giving V_s. For the aqueous cell

$$Q_{AQ} = \frac{(V_P/V_s)_{AQ}}{\frac{2}{3}(V_P/V_s)_{REF_1} + \frac{1}{3}(V_P/V_s)_{REF_2}} \tag{1}$$

and for the organic cell

$$Q_{ORG} = \frac{(V_P/V_s)_{ORG}}{\frac{1}{3}(V_P/V_s)_{REF_1} + \frac{2}{3}(V_P/V_s)_{REF_2}} \tag{2}$$

A normalised voltage V_P/V_S is proportional to the integrated photon flux at the face of the phototube. This flux consists of two kinds of gamma photons—those which have passed through the cell solution and those which have not. Assuming an average in-solution path length, Beer's Law gives a simple mathematical representation of the flux from the former as a function of the uranium concentration of the solution. Also, assuming that a particular cell is always placed in the same position in the absorptiometer, the flux from the latter is constant. The resulting law is

$$V_P/V_s = A + Be^{-c[U]} \tag{3}$$

where [U] is the uranium concentration of the solution in g/l. The three constants A, B, and c in equation (3) are identified with scattering, solvent, and uranium attenuation, respectively. Here, *scattering* is an omnibus term covering the total geometry of the cell and the experimental apparatus, and the scattering properties of air and apparatus materials. The parameter c depends only on the average in-solution path length and the physics of attenuation of americium-241 gamma photons by uranium atoms. The parameters A and B, on the other hand, fluctuate with instrument shifts. However, A/B should be time invariant, depending only on the cell, solvent and experimental apparatus. The solvent effect should only be present in B. For a reference cell filled with distilled water, equation (3) reduces to

$$(V_P/V_s)_{REF} = A' + B' \tag{4}$$

When a sample cell and the reference cell are analysed alternately the A and B sample cell parameters and the A′ and B′ reference cell parameters will fluctuate as a set, any two remaining in a fixed ratio. Thus, for each sample cell the ratio

$$Q = \frac{(V_P/V_s)_{SAMPLE}}{(V_P/V_s)_{REF}}$$

should satisfy

$$Q = a + be^{-c[U]} \tag{5}$$

where

$$a = A/(A' + B') \text{ and } b = B/(A' + B').$$

Equation (5) will be called the *modified Beer's law*. Assuming good experimental procedure, *a* should depend only on the sample cell and *b* only on the sample cell and the solvent. Hence, for identical cells and a single solvent *a* and *b* should be the same. Following the calibration of a particular sample cell for aqueous uranium solutions, organic uranium solution calibration should entail only replacing "*b*" by

$b' = b\varepsilon$, where *log* ε is the *zero shift* from aqueous to organic solvents. The experiments discussed in the sequel were designed to test these assumptions for two different sample cell sizes and to estimate the aqueous and organic calibration functions.

In the data reduction, the uranium concentrations are found directly from the inverse function of (5), expressing uranium in terms of Q and calibrated parameters. The volumetric fraction of organic phase in the sample is easily found after the burette readings are regenerated from V_{R_0}, V_{R_1} and V_{R_2}. The amount of nitric acid in the aqueous phase is determined, by means of the *HpH* method which has been described,[2] from the pH (which is directly calculated from V_{pH}) and the uranium in the aqueous phase.

Aqueous cell calibration

The purpose of the aqueous cell calibration experiment was to calibrate as precisely as possible the four aqueous and organic sample cells over a uranium concentration range of 0 to 120 g/l. The experiment was designed so that individual calibration functions, expressing uranium concentration in terms of the ratio of the sample cell to reference cell voltage ratios Q, could be determined for each sample cell; further, that a statistical test could be performed to decide whether a single calibration function could be used for sample cells with a common path length; and finally, that the accuracy of the method could be estimated as a function of uranium concentration.

The experimental data were collected in such a manner that a preliminary analysis could be performed to check the stability of the ratio of standard voltage to integration time (V_S/T), to check the stability of the reference cell voltage ratio $(V_P/V_S)_{REF}$ and to allow correction of the data for drift over the entire experimental period.

The fundamental unit in the experimental design for the aqueous calibration (as shown in Table II) was the *loading*. The design consisted of 20 of these loadings. A *loading* specifies both the uranium standard solution used in each of the four sample cells and the order in which these cells are analysed on the absorptiometer. Within a loading, four different uranium standard solutions were used, one to each of the four sample cells. The analysis schedule consisted of 13 independent analyses. Hereafter, the words *sequence position* are used to identify the 13 ordered spots in this schedule. The reference cell was analysed five times for each loading in sequence positions 1, 4, 7, 10 and 13. Between each pair of reference cell analyses, two distinct sample cells were each analysed once. Thus, the complete analysis schedule for a loading always involved five reference cell analyses and two analyses

TABLE II.—AQUEOUS CALIBRATION EXPERIMENTAL DESIGN

Loading number	Analysis sequence within a loading												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1	R	A-0	B-1	R	C-2	D-3	R	B-1	D-3	R	A-0	C-2	R
2	R	B-6	D-4	R	A-1	C-0	R	A-1	B-6	R	C-0	D-4	R
3	R	B-7	A-2	R	D-6	C-9	R	D-6	B-7	R	C-9	A-2	R
4	R	D-8	B-0	R	C-6	A-3	R	B-0	A-3	R	D-8	C-6	R
5	R	A-4	C-7	R	B-5	D-9	R	C-7	D-9	R	A-4	B-5	R
6	R	C-1	D-2	R	A-5	B-4	R	A-5	C-1	R	B-4	D-2	R
7	R	C-5	A-6	R	D-1	B-8	R	D-1	C-5	R	B-8	A-6	R
8	R	D-5	C-8	R	B-2	A-7	R	C-8	A-7	R	D-5	B-2	R
9	R	A-8	B-9	R	C-3	D-0	R	B-9	D-0	R	A-8	C-3	R
10	R	A-9	C-4	R	B-3	D-7	R	C-4	D-7	R	A-9	B-3	R
11	R	B-5	D-7	R	A-4	C-6	R	A-4	B-5	R	C-6	D-7	R
12	R	C-5	D-8	R	A-7	B-2	R	A-7	C-5	R	B-2	D-8	R
13	R	C-4	A-5	R	D-0	B-1	R	D-0	C-4	R	B-1	A-5	R
14	R	B-4	A-9	R	D-1	C-2	R	D-1	B-4	R	C-2	A-9	R
15	R	D-3	C-0	R	B-6	A-8	R	C-0	A-8	R	D-3	B-6	R
16	R	D-6	B-8	R	C-9	A-3	R	B-8	A-3	R	D-6	C-9	R
17	R	A-0	B-3	R	C-7	D-9	R	B-3	D-9	R	A-9	C-7	R
18	R	B-9	C-3	R	D-4	A-6	R	D-4	B-9	R	C-3	A-6	R
19	R	C-1	D-5	R	A-2	B-7	R	A-2	C-1	R	B-7	D-5	R
20	R	D-2	A-1	R	B-0	C-8	R	C-8	A-1	R	D-2	B-0	R

TABLE III.—AQUEOUS URANIUM STANDARD SOLUTIONS

Identification	Concentration, *g/l.*
0	Pure distilled water
1	1·018
2	4·990
3	10·044
4	20·046
5	40·324
6	59·903
7	81·364
8	100·544
9	120·642

of each sample cell. Barring drift in the absorptiometer, the two analyses of a sample cell were duplicates because the uranium solutions were not changed within a loading. In the complete schedule of 20 loadings, every sample cell was analysed twice when filled with each of the 10 uranium standards. For each analysis on the absorptiometer, the month, the day and time of the analysis, the loading number, the sequence position number, the cell identification number, the uranium standard solution identification number and the absorptiometer data triplet V_p, V_s and T were recorded.

The complete experimental design is listed in Table II. The letters identify cells—R is the reference, A and B the 1-cm path length cells, and C and D the 5-cm path length cells. The numbers identify standard solutions in order of increasing uranium concentration—Table III gives the specific correspondence. The letter number pairs (A–0, *etc.*) in Table II indicate cell-solution pairings for each loading.

The experimental data were collected on three consecutive days in agreement with the experimental design as depicted in Table II. Loadings 1–5 were done on day 1, 6–13 on day 2 and 14–20 on day 3. The average experimentation time per loading was about 42 min–12 min to clean, dry and fill four sample cells, and 30 min to do the sequence of 13 analyses. Of the 2¼ min/analysis, approximately 1 min (61·7 sec) was actual absorptiometer integration time.

The standard solutions with concentrations given in Table III were made up from crystalline uranyl nitrate hexahydrate (UNH). Enough concentrated nitric acid was added to make each solution 10 g/l. in nitric acid. The standards were analysed according to a method described by Brouns.[1] The method briefly consists of : (1) pipette an aliquot of the standard solution into a weighed crucible, (2) evaporate to dryness, (3) ignite to U_3O_8 and (4) weigh crucible and content. Variation between two similar analyses of the same standard solution by this method was never greater than 0·3%. This analysis procedure was repeated three times for each standard solution. The values quoted in Table III are the averages of the three determinations. At the 95% confidence level, the precision of these averages is about 0·027 g/l.

STATISTICAL ANALYSIS OF AQUEOUS CELL CALIBRATION

In order to estimate the stability and drift characteristics of the absorptiometer, a preliminary statistical analysis (see p. 316 to 317) was done with data from 100 reference cell readings. In summary, the standard deviation of the 100 standard voltage-integration time ratios (V_s/T) was 0·000189, approximately 0·1% of the average reading of —0·18377. From a practical standpoint, variability of this magnitude is minor compared to other errors in the measurement processes. Even so, insight into the standard voltage measurement process is gained from analysis of this variability. In Fig. 3 the plot of the 20 loading averages shows that the (V_s) voltage signal drifts continuously with time. Fig. 4 shows the sequence position (V_s/T) ratios averaged over the 20 readings. The total decay during the reading of five sequence positions is about 0·08% of the average (V_s/T) reading. The short term random fluctuation in the voltage signal has a standard deviation of 0·00003, less than 0·02% of the average signal.

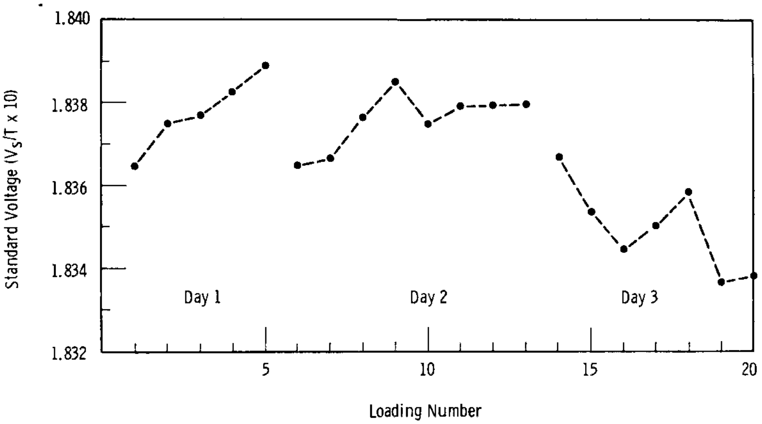

FIG. 3.—Variation of standard voltage with loading.

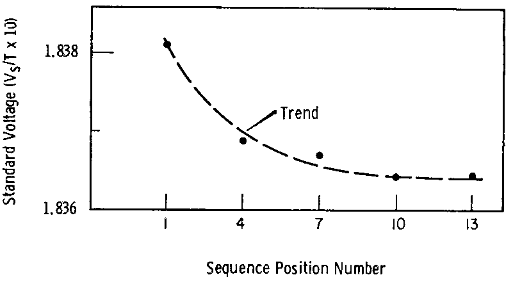

FIG. 4.—Variation of standard voltage with sequence position.

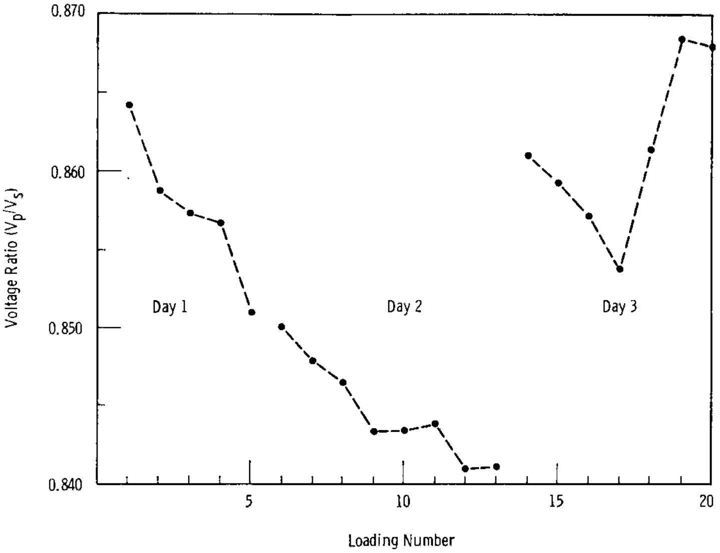

FIG. 5.—Variation of reference cell voltage ratio with loading.

The reference cell voltage ratios (V_P/V_s) were also statistically analysed (see p. 317). The results were similar to that for the (V_s/T) data. Fig. 5 is a plot of the 20 loading averages and Fig. 6 a plot of the five sequence positions averaged over loadings. The long term drift in the (V_P/V_s) response could presumably arise from the gradual change in phototube sensitivity and source decay. For 2–$\frac{1}{2}$ of the 3-day experimental period the ratio (V_P/V_s) steadily decreased. Fig. 6 shows a significant within-loading decay similar to that of the (V_s/T) data. The standard deviation of the short term random fluctuation in the (V_P/V_s) signal is 0·00223. The average of the 100 (V_P/V_s) readings is 0·85374; hence, the standard deviation of the residual variability or noise in the (V_P/V_s) signal is about 0·25% of its average. On a relative basis the noise in the (V_P/V_s) signal for the reference cell is about 15 times as great as in the (V_s/T) signal.

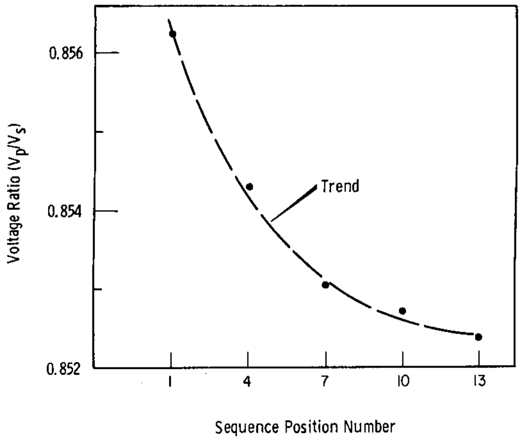

FIG. 6.—Variation of reference cell voltage ratio with sequence position.

There is no evidence that the (V_P/V_s) and (V_s/T) reference cell ratios are correlated. Probably any correlation resulting from the common component (V_s) is masked by the extreme variability in (V_P).

To eliminate as much as possible the time effect in the basic (V_P/V_s) absorptiometer reading, sample cell data were normalised with a linearly interpolated reference cell response from readings taken immediately before and after that of the sample cell pair (see p. 317). For the experimental schedule (see Table II) used for the aqueous calibration, the appropriate weighting factors are either ($\frac{2}{3}$, $\frac{1}{3}$) or ($\frac{1}{3}$, $\frac{2}{3}$) depending upon which reference cell, pre- or post-, is juxtaposed to the sample cell in the analysis schedule. In either case, the normalised sample cell reading has the form

$$Q_{\text{SAMPLE}} = \frac{(V_P/V_s)_{\text{SAMPLE}}}{(\frac{1}{3})(V_P/V_s)_{\text{REF}_1} + (\frac{2}{3})(V_P/V_s)_{\text{REF}_2}} \tag{6}$$

The normalisation equation (6) is the same as (1) and (2) above. The distinction is in the application because (6) applies to the aqueous calibration data while (1) and (2) apply to routine analysis of aqueous and organic solutions. Assuming that the noise, on a relative basis, in the sample cell ratio $(V_P/V_s)_{\text{SAMPLE}}$ is about the same as that seen in the reference cell ratio and that the time effect in the absorptiometer is removed by the normalisation, the standard deviation of the sample cell normalised reading Q_{SAMPLE} will be approximately 0·31%. This figure of 0·31% considers only the precision with which the *in situ* sample cell uranium concentration is estimated. In general, when the concentration of an aqueous uranium solution is measured with the gamma absorptiometer, additional errors may be involved which are completely independent of the absorptiometer analysis processes, *e.g.*, residual contamination in the sample cell. If such is the case, the standard deviation of the total error could well be much greater than 0·31%. Also, there is no guarantee that the standard deviation will remain 0·31% over the entire uranium range of interest. For trace uranium concentrations the standard deviation certainly will increase.

The 160 sample cell voltage ratios (V_p/V_s), 40 for each of the four cells, A, B, C and D, were normalised with adjacent reference cell data as in equation (6). The normalised data were analysed statistically to determine whether the normalisation process eliminated the time trend seen in the reference cell (V_p/V_s) data, and whether path length was the only characteristic of the four sample cells which affected the absorptiometer reading. The details of the analysis are included on p. 317 to 318. The analysis indicated no significant time effect in the Q_{SAMPLE} values, so that the normalisation process proved successful. Data from the two 1-cm path length cells A and B appeared to be replicates using a single cell, as did the data from the two 5-cm path length cells C and D.

As a result, the entire set of normalised ratios were expressed as 20 averages, each involving all readings using cells of the same path length and filled with the same uranium solution. The remaining degrees of freedom estimated the replication error about these averages. The replication standard error was approximately 0·0012 in absolute units. It did not depend on sample cells or on uranium concentration. In relative units it increased from 0·12% to 0·25% for the 1-cm cells and from 0·12% to 5·0% for the 5-cm cells over the entire concentration range of 0 to 120 g/l. The reference cell analysis prediction of 0·31% standard error in these normalised Q values was significantly greater than the above figure of 0·12% for zero uranium concentration Q values. Because sample cells with water only should behave exactly as the reference cell, normalisation actually removed (in addition to the time effects) some of the short term variability classified as random in the reference cell analysis. Implicit in this statement also is that there was no evidence of residual solution contamination in the sample cells or any other loading effect. All 20 averages are plotted as points using a logarithmic scale against uranium concentration in Fig. 7. A linear relationship in these points is in agreement with Beer's law, equation (5) with the scattering parameter $a = 0$. The 1-cm cell data are approximately linear. However, the 5-cm cell data clearly deviate from a linear relationship, indicating the necessity of a scattering parameter in the model.

The modified Beer's law (5) was fitted to the 10 plotted points for each cell size. The details of the estimation are on p. 318. The resulting aqueous calibration functions for the two cell sizes are listed in Table V. These functions are the inverses of the modified Beer's law estimates, expressing uranium concentration explicitly in terms of Q. In Fig. 7 the model appears to fit the data adequately. However, statistical analysis (see p. 318 and Table IV) shows that the model fit is quite poor for two uranium solutions. Errors of 0·200 g/l in the standard values of

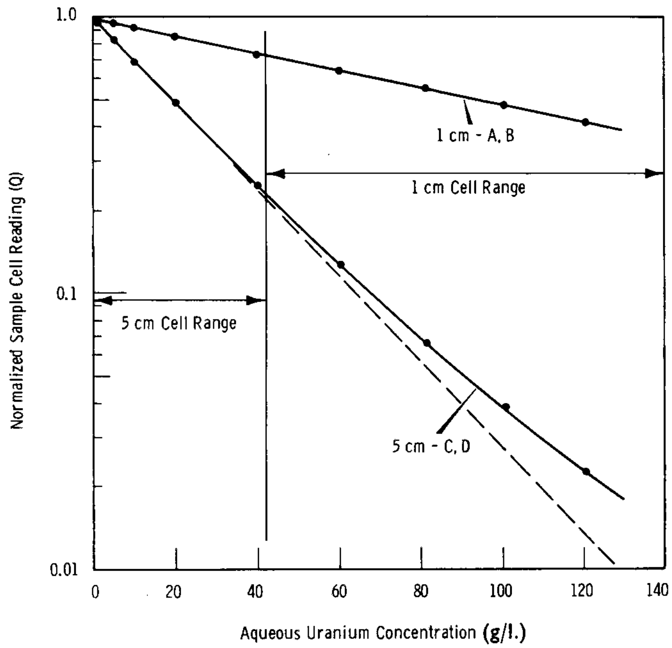

FIG. 7.—Aqueous cell calibration data and modified Beer's law.

TABLE IV.—ANALYSIS OF VARIANCE-SAMPLE CELL CALIBRATION

Source	Sum of squares ($\times 10^6$)		Degrees of freedom	Mean squares ($\times 10^6$)	
	5-cm cell	1-cm cell		5-cm cell	1-cm cell
Uranium					
Calibration	11,308,297·6260	3,444,594·8437	2		
Residual	194·0300	43·0100	7	27·7186	7·1443
Cells	0·6661	0·0500	1	0·6661	0·0500
Interaction	8·7252	21·8525	9	0·9695	2·4281
Replication	84·1700	86·2940	60 56[a]	1·4028	1·5410
TOTAL	11,308,585·2173	3,444,746·0502	79 75		

[a] Four outlier observations were deleted from the 1-cm cell analysis.

TABLE V.—AQUEOUS URANIUM SOLUTION CALIBRATION FUNCTION

Concentration range, *g/l.*	Function, *g/l.*	Accuracy limits,[a] *g/l.*
	For 1-cm path length	
40–120	$U = 127{\cdot}1 \log_e \left(\frac{0{\cdot}9412}{Q - 0{\cdot}0554}\right)$	0·27–0·50
	For 5-cm path length	
0–40	$U = 27.70 \log_e \left(\frac{0{\cdot}9829}{Q - 0{\cdot}0126}\right)$	0·07–0·27

[a] Standard deviation of uranium concentration estimate.

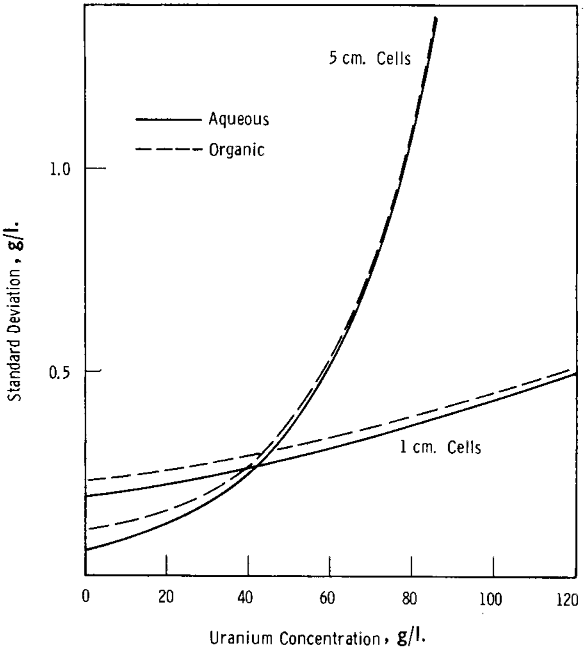

FIG. 8.—Accuracy of aqueous and organic uranium solution analysis using modified Beer's law calibration function.

these solutions would explain the significance. Fig. 8 is a plot of the accuracy of the aqueous uranium solution estimation as a function of uranium concentration. Accuracy is expressed as total standard deviation in g/l., which includes both the random error in an individual Q ratio and the deviation between the model and standard solutions. For both size cells the total standard deviation increases with uranium concentration. The 5-cm cells are more accurate for low concentration and the 1-cm ones for high. The crossover point is about 40 g/l. The accuracy limits for each calibration function over the range of uranium concentration for which it has the smaller total standard deviation are listed in Table V. Using 42 g/l. as the point for switching from 5-cm cells to 1-cm cell gives analysis accuracy of 0·2 g/l. at zero with a monotone increase to 0·5 g/l. at 120 g/l.

Details of statistical analysis

The 100 standard voltage-integration time ratios (V_S/T) obtained from the reference cell analysis, were analysed with a two-factor (loading at 20 levels and sequence

TABLE VI.—ANALYSIS OF VARIANCE—(V_S/T) REFERENCE CELL DATA

Source	Sum of squares ($\times 10^6$)		Degrees of freedom		Mean sum of squares ($\times 10^6$)	
Loading	3·06116		19		0·16111	
Between days		2·03001		2		1·01500
Within days		1·03115		17		0·06066
Sequence position	0·38250		4		0·09563	
Residual	0·09997		76		0·00132	
Error		0·03142		38		0·00087
Remainder		0·06857		38		0·00180
TOTAL	3·54363		99		0·03579	

position at 5 levels) completely crossed analysis of variance. Loading was a random factor and sequence position a fixed factor. Table VI shows the breakdown of the total variation in the (V_s/T) ratios. The 19 degrees of freedom for loading are partitioned into between days and within days effects. Also, 38 degrees of freedom, called *error* are broken out of the residual sum of squares. The error sum of squares measures the variation in the differences between adjacent sequence positions (1–2 and 10–13) across the 20 loadings. This variation should better approximate the variability associated with linearly interpolated values than the residual variance, because the latter is really a measure of the non-additivity of the model rather than a true error estimate.

Clearly, days are the major contribution to the voltage variability. Fig. 3 shows that there is no physical day effect in the loading averages. Both between and within days mean squares are measuring the same voltage drift. Sequence position also is a significant effect as discussed in the main text. The error mean square is significantly smaller than the remainder mean square which indicates that the residual mean square overestimates the short term random fluctuation in the voltage signal. Using the error mean square gives a standard deviation of 0·00003.

The 100 reference cell voltage ratios (V_P/V_s) were analysed in exactly the same manner as the (V_s/T) voltage data discussed above. The analysis of variance breakdown is shown in Table VII. The conclusions from the analysis are similar to those for the (V_s/T) data except that the sequence position and error mean squares are, though significant, less significant than for the (V_s/T) data. The error mean square gives a standard deviation of 0·00223 for the short term random fluctuation.

TABLE VII.—ANALYSIS OF VARIANCE—(V_P/V_S) REFERENCE CELL DATA

Source	Sum of squares ($\times 10^6$)		Degrees of freedom		Mean sum of squares ($\times 10^6$)	
Loading	7371·60		19		387·98	
Between days		5861·53		2		2840·77
Within days		1690·07		17		99·42
Sequence position	198·74		4		49·69	
Residual	40·53		76		7·12	
Error		188·73		38		4·97
Remainder		351·80		38		9·24
TOTAL	8110·87		99		81·93	

The 80 sample cell normalised Q ratios for A and B 1-cm path length cells and the 80 for the C and D 5-cm path length cells were each analysed with a two factor (uranium at 10 levels and cells at 2 levels) completely crossed analysis of variance with four replicate observations at each of the 20 two-factor level combinations. Uranium was a random factor and cells a fixed factor. Table IV shows the results of the analysis. Four outlier observations from the 1-cm cell data were replaced by three-replicate averages based on significantly large replicate variance. In both analyses the cells main effect and cells-uranium interaction were not significant compared to replicate error. Thus, the A and B cells and the C and D cells could be treated as identical in the calibration. A supplementary analysis which regressed the additive model residuals on loading and sequence position showed that the Q ratio normalisation successfully removed the time effect in the absorptiometer response.

For each cell size the 10 uranium level averaged Q ratios (each average was over eight individual Q values) were fitted to the modified Beer's law (5) by least squares. The least squares parameter estimation was done by an iterative non-linear least squares programme on the Hanford IBM–7090 computer. In Table IV the 9 degrees of freedom for uranium are partitioned by this estimation into 2 explained by the modified Beer's law, called *calibration*, and 7 measuring the variation in the average Q ratios about the calibration function, called *residual*. For both size cells the residual mean square is too large to be explained by random error, so that neither calibration function explains all the uranium level connected variation in the data. The major contributors to the two residual mean squares are the highly significant positive residuals at 10·044 g/l. and negative residuals at 120·642 g/l. A shift of 0·200 g/l. in each of these two standard values would explain the significance.

ORGANIC CELL CALIBRATIONS

Because of the difficulties inherent in preparing organic phase standard solutions, a method to calibrate the absorptiometer for organic solutions was desired which used only aqueous phase standards. The modified Beer's law (5) implies that the absorptiometer response $\log_e (Q_{ORG} - a)$ for organic liquids and the response $\log_e (Q_{AQ} - a)$ for aqueous liquids differ by only a constant due to the incremental change in the solvent mass absorption coefficient (hereafter this effect is termed *organic zero shift*). The following method may be used to check this zero shift theory:

(1) Mix 50 ml of organic solvent with 50 ml of one of the aqueous standard uranium solutions (see Table III). (2) Allow the mixture to equilibrate and separate the two phases. (3) Analyse both phases independently on the absorptiometer using the same sample cell to obtain $\log_e (Q_{AQ} - a)$ and $\log_e (Q_{ORG} - a)$. (4) Repeat 1, 2 and 3 for several different aqueous standards (in the experiment the four standards, distilled water, 40·234 g/l., 81·364 g/l. and 120·642 g/l. were used).

When a mixture equilibrates, the exact uranium concentration of each phase is not known. However, because equal volumes of aqueous and organic went into the mixture, the sum of the uranium concentrations of the two phases is the same as that of the aqueous standard originally used in the mixture. If the zero shift theory is correct, the model

$$\log_e (Q_{AQ} - a) + \log_e (Q_{ORG} - a) = 2\log_e b + \log_e \varepsilon + cU_T \qquad (7)$$

is applicable for each aqueous standard uranium concentration U_T and should fit the data as well as the modified Beer's law (5) fits the aqueous calibration experimental data. Moreover, the least squares estimate of the slope parameter c obtained by regressing $\log_e (Q_{AQ} - a) + \log_e (Q_{ORG} - a)$ on U_T should not differ significantly from the slope estimate of c calculated from the aqueous calibration data (see Table V). Once the zero shift theory has been checked, the proper ε parameter is directly estimated from the zero uranium concentration data.

An organic cell calibration experiment was designed to use the above method with the following purposes in mind:

1. Determine whether the organic shift theory is substantiated according to the above criteria.
2. If substantiated, estimate the magnitude of the shift $\log_e \varepsilon$ in equation (7) from the zero uranium data.

3. Calculate the precision of the estimate of $\log_e \varepsilon$.
4. Determine the precision with which uranium concentration in the organic phase can be assayed by gamma absorptiometry, when the calibration is accomplished by zero shifting the aqueous calibration for the same instrument.

The organic-phase solvent used in the pulse column test facility consists of 30% by volume of tributyl phosphate (TBP) in a kerosene-type diluent. The organic liquids for the calibration of the absorptiometer were prepared by taking a 2-l. aliquot of this solvent and scrubbing it in the following manner to remove any possible traces of uranium. First, contact organic with 25 g of sodium carbonate in 500 ml of distilled water and decant the aqueous phase. Second, contact organic with 50 ml of 60% nitric acid in 500 ml of distilled water and decant aqueous phase. Third, wash organic with distilled water. The above process was repeated 4 times to obtain the first organic liquid O_1 and 5 times to obtain the second liquid O_2. The experimental design for the organic calibration included these two organic liquids so that a check was possible on their purity.

The above procedure gave water-saturated organic liquids for calibration. It was necessary to ensure that the organic was saturated with water before the equilibrations with uranium-containing aqueous phase standards because water is soluble to the extent of 0·39 ml in 50 ml of the TBP-kerosene.[4] The solubility of the organic solvent in the aqueous is negligible by comparison, being only $2{\cdot}5 \times 10^{-4}$ ml in 50 ml of aqueous phase.[4]

The experimental design (see Table VIII) for the organic calibration was a complete 2 × 4 factorial with two equilibrations in each cell. The two factors of the factorial were: (1) organic liquid at two levels, O_1 and O_2, and (2) aqueous uranium solution concentrations at the four levels mentioned above which were designated 0, 1, 2, 3. For each pairing of an organic level and a uranium concentration level, a single equilibration and the resulting separated organic and aqueous phases constitute a unit. Two such units were scheduled for each of the eight paired levels of the factorial design so that a check would be possible on the precision of the equilibration-separation process. Thus, the entire experimental schedule involved 16 independent units. In Table VIII, the unit is identified with the equilibration number in the order in which the absorptiometer analyses were performed. The second and third columns in Table VIII give the paired levels for the equilibration.

TABLE VIII.—ORGANIC CALIBRATION EXPERIMENT DESIGN

Equilibration number	Organic liquid	Aqueous uranium standard solution concentration
1	O_1	0
2	O_2	1
3	O_1	2
4	O_2	3
5	O_2	2
6	O_1	3
7	O_2	0
8	O_1	1
9	O_2	3
10	O_1	2
11	O_2	1
12	O_1	0
13	O_1	1
14	O_2	0
15	O_1	3
16	O_2	2

The analysis of an equilibration was always done in the same manner:

(1) Fill the A cell (1-cm path length) and the D cell (5-cm path length) with the separated aqueous phase. (2) Run the analysis sequence RDARADR on the absorptiometer (here, R is the same 5-cm path length distilled water reference cell as used in the aqueous calibration), and record data as for an aqueous calibration loading. (3) Empty, clean and fill A and D cells with separated organic phase. (4) Run the analysis sequence RADRDAR and record as for (2) above.

STATISTICAL ANALYSIS OF ORGANIC CALIBRATION DATA

In order to determine whether the equilibration-separation process was reproducible and whether trace uranium was still being removed from the organic liquid by the fifth scrubbing, a preliminary analysis of variance calculation was performed on the organic calibration data. The details of the analysis are discussed on p. 322 to 323.

The results of the analysis, as summarised in Table IX, indicate that the absorptiometer stability during the organic calibration was similar to that during the aqueous calibration. The 5-cm path length cell data show a significant decrease in the Q ratios for O_2 solvent over corresponding uranium concentration Q ratios for O_1 solvent. In physical units, this decrease corresponds to the removal of 0·04 g/l. uranium during the fifth scrub. A change in uranium concentration of this magnitude could not be detected with the 1-cm path length A cell. Data for both cells show that the ratio of the organic to aqueous uranium concentration is a function of uranium concentration (this effect appears as a solvent-uranium interaction in the analysis of variance Table XI). This was to be expected and was what prompted the addition model (7) analysis. A more subtle effect was that there was a small but significant difference between the ratios for the two organics for the three positive uranium concentration levels. (This effect appears as a solvent-uranium-organic interaction

TABLE IX.—ANALYSIS OF VARIANCE—ORGANIC ZERO SHIFT

Source	Sum of squares ($\times 10^4$)		Degrees of freedom		Mean sum of squares ($\times 10^4$)	
	1-cm cell	5-cm cell	1-cm cell	5-cm cell	1-cm cell	5-cm cell
Regression	20,051·6682	412,382·2937	1	2	20,051·6682	206,191·1468
Residual	0·0988	13·7915	2	5	0·494	2·7583
Sub-total	20,051·7670	412,396·0852	3	7		
Replication	0·2708	1·4574	12	8	0·0226	0·1822
TOTAL	20,052·0378	412,397·5426	15	15		

TABLE X.—ORGANIC URANIUM SOLUTION CALIBRATION FUNCTION[a]

Concentration range, *g/l.*	Function, *g/l.*	Accuracy limits,[b] *g/l.*
	1-cm path length	
45–120	$U\ 127{\cdot}1 \log_e \left(\frac{0{\cdot}9502}{Q - 0{\cdot}0554}\right)$	0·31–0·52
	5-cm path length	
0–45	$U = 27{\cdot}70 \log_e \left(\frac{b}{Q - 0{\cdot}0126}\right)$	0·12–0·31

[a] b = 1·0547 for O_1 solvent,
b = 1·0585 for O_2 solvent.

[b] Standard deviation of uranium concentration estimate.

in the analysis of variance.) This difference did not change with uranium concentration. A simple explanation is that the two organics had different nitric acid concentrations. No attempt was made to determine the organic acid concentration nor to stabilise it during the scrubbing process. Finally, the preliminary analysis indicated that the equilibration-separation process was reproducible; in fact, the difference between the two duplicates was uniformly explainable in terms of the fundamental absorptiometer replication error.

The 128 sample cell normalised Q ratios were split into A and D cell groups. Each group of data was reduced to 16 observations, one for every equilibration. First, the appropriate a scattering parameter was used to calculate $\log_e (Q - a)$ for each Q ratio, then the two replicate analyses for each phase were averaged to give a single $\log_e (Q_{AQ} - a)$ and $\log_e (Q_{ORG} - a)$ for each equilibration. These average logarithms were added to give the single observation,

$$\log_e (Q_{AQ} - a) + \log_e (Q_{ORG} - a),$$

for each equilibration. The organic distribution ratio interaction present in the individual $\log_e (Q - a)$ readings was summed out of the data by this addition process and did not affect the check on the zero shift theory. The regression model of equation (7) was fitted by least squares to the 16 data points

$$[\log_e (Q_{AQ} - a) + \log_e (Q_{ORG} - a), U]$$

where U, the independent variable, was the aqueous standard uranium concentration. The regression analyses are discussed on p. 19 and summarised in the analysis of variance table of Table IX.

The results of the analysis indicate that the organic calibration data fit the modified Beer's law as well as the aqueous calibration data. The estimates of the attenuation parameter c in the zero shift model (7), given in the form $-1/c$, are 127·3 and 28·05 for the A and D cells, respectively. These are not significantly different from the aqueous calibration function parameters 127·1 and 27·70 of Table V. Thus, both the fit of the zero shift model and the estimates of the attenuation parameter do not refute the organic zero shift theory for either cell.

The organic zero shift parameters $\log_e \varepsilon$ in (7) were estimated from the zero uranium concentration data with the formula,

$$\log_e \varepsilon = \overline{\log (Q_{ORG} - a)} - \overline{\log_e (Q_{AQ} - a)} \qquad (8)$$

Here, the "bar" indicates average over-all appropriate $\log_e (Q - a)$ replicates. For the 1-cm path length A cell the averages each involve eight replicates. For the 5-cm path length D cell individual zero shift parameters were estimated for the two organic solvents O_1 and O_2, so the averages each involved four replicates. The weighted average of these estimates corresponds to −4·16 g/l. and −4·20 g/l. for the O_1 and O_2 organic solvents, respectively. The standard deviations of the resulting calibration function shifts are 0·14 g/l. for the A cell and 0·90 g/l. for the D cell. The organic uranium solution analysis accuracy of these calibration functions is plotted as the dash curves in Fig. 8. The difference between the dash and solid curves is the additional inaccuracy resulting from the zero shift method of adjusting an aqueous calibration function to give the organic one. From Fig. 8, the change-over point between cells is 45 g/l. for organic analysis. The organic uranium solution functions are listed in Table X along with accuracy limits for their recommended concentration range.

TABLE XI.—ANALYSIS OF VARIANCE—PRELIMINARY ORGANIC ANALYSIS

Source	Sum of squares ($\times 10^4$)		Degrees of freedom	Mean sum of squares ($\times 10^4$)	
	1-cm cell	5-cm cell		1-cm cell	5-cm cell
MODEL					
Uranium	20,051·7670	412,391·4096	3	6,683·9220	137,463·8032
Organic	0·0819	4·3203	1	0·0819	4·3203
Uranium-organic interaction	0·0321	0·3553	3	0·0107	0·1184
Equilibration	0·2387	1·4574	8	0·0298	0·1822
PHASE DISTRIBUTION					
Solvents	273·2753	5,743·9952	1	273·2753	5,743·9952
Solvent-uranium interaction	351·9959	6,986·9578	3	117·3320	2,328·9859
Solvent-organic interaction					
Uranium present	4·7969	100·2786	1	4·7969	100·2786
Residual	0·1941	0·3379	3	0·0647	0·1126
Equilibration	0·2321	1·5129	8	0·0290	0·1891
REPLICATION	1·5758	6·0841	31	0·0493	0·1901

Details of statistical analysis

The 128 sample cell voltage ratios $(V_P/V_s)_{AQ}$ and $(V_P/V_s)_{ORG}$ formed from the organic calibration experiment were normalised with interpolated reference cell voltage ratios $(V_P/V_s)_{REF}$ using (6). The normalised ratios Q_{AQ} and Q_{ORG} were adjusted with appropriate scattering parameters and natural logarithms were calculated to form a set of 32 pairs of $[\log_e (Q_{AQ} - a), \log_e (Q_{ORG} - a)]$ data for each cell size, one pair for every equilibration separation. The model for the sum of the components of each pair is given by (7). The model for difference of the components is

$$\log_e (Q_{AQ} - a) - \log_e (Q_{ORG} - a) = -\log_e \varepsilon + c(U_{AQ} - U_{ORG}) \qquad (9)$$

For each cell size the sums of the 32 pairs and the differences of the 32 pairs were each analysed with a three-factor (uranium at four levels, organic at two levels, and equilibrations at two levels) design. Uranium and organic were crossed and equilibrations nested in each uranium-organic pairing. The analysis of variance breakdown for the design is given in Table XI. The two replicates for each equilibration give 16 degrees of freedom for sums and 16 for differences for each cell size. In the absorptiometer analysis schedule half of one run was not recorded. Therefore, one replicate degree of freedom was lost for differences with each cell. Sums and differences replicate sum of squares were pooled to give a replicate mean square with 31 degrees of freedom. Equation (7) shows that the sums data for a cell should depend linearly on the uranium concentration and the organic shift parameter. The top half of Table XI, marked "MODEL", gives the appropriate variance breakdown. For both cell sizes, equilibration and uranium-organic interaction mean squares are not significant. For the 1-cm cell the organic mean square is not significant but for the 5-cm cell it is very significant. The non-significant interaction implies that equation (7) is an adequate representation of the sum data. The physical interpretation of the organic and equilibration non-significance is discussed in the main text.

Equation (9) shows that the difference data for a cell should depend linearly on the organic shift and on the difference between the equilibrated aqueous and organic-uranium concentrations, the phase distribution. The average difference for a cell should be just a linear combination of the average organic shift and the average phase distribution. The bottom half of Table XI, marked "PHASE DISTRIBUTION", gives the appropriate variance breakdown. The solvent mean square measures the average difference between the phases, *i.e.*, the average value of the model (9). The highly significant result is largely due to the concentration increment $U_{AQ} - U_{ORG}$ because the zero shift $\log_e \varepsilon$ is numerically quite small. The significant solvent-uranium interaction means that the $U_{AQ} - U_{ORG}$ changes with total uranium concentration. In the customary breakdown, the 4 degrees of freedom for solvent-organic interaction would be partitioned into one for solvent-organic interaction and three for solvent-organic-uranium interaction. In such a breakdown both mean squares would be significant. The breakdown of the sums of squares in Table XI places all the significance in 1 degree of freedom, the average solvent-organic interaction over the three positive uranium concentration levels. Thus, when uranium is present, the concentration increment $U_{AQ} - U_{ORG}$ is different for the two organics O_1 and O_2; however, the increment is independent of the exact amount of uranium present.

The non-significance of the equilibration mean square means that the phase distribution was reproducible in the two separate equilibration-separation processes.

For each cell size the 15 degrees of freedom associated with MODEL were fitted by least squares to the regression function (7) with total uranium concentration U as a covariate. For the 5-cm cell a parameter was included for the significant organic effect. Table IX gives the variance breakdown for the regression analysis. For the 5-cm cell the regression-residual partition splits the 7 degrees of freedom associated with uranium, organic, and uranium-organic interaction in Table XI. The replication is measured by the 8 degrees of freedom between equilibrations. For the 1-cm cell the 4 degrees of freedom associated with organic and uranium-organic interaction are pooled with equilibrations to measure replication. The regression-residual partition splits the 3 degrees of freedom associated with uranium. The residual mean squares indicate that the model (7) fits the sum data to 0·2% and 1·7%, respectively, for the 1-cm and 5-cm cells. These percentage figures are in good agreement with the percentage ranges of the aqueous calibration data fit to the modified Beer's law (5).

DISCUSSION OF ERRORS IN CALIBRATIONS

The analysis of the aqueous and organic calibration has demonstrated that the accuracy of the absorptiometer for either organic or aqueous phases varies from 0·1 to 0·5 g/l. over the uranium concentration range of 0 to 120 g/l. This is because of the variability or random noise inherent in an *in situ* uranium estimation.

In order to isolate the source of this variability, the variabilities in the four major components of the absorptiometer system were looked at in more detail. These components are:

1. The integrating picoammeters [which give (V_P) and (V_S)] which includes all variability from capacitance changes, amplifier gain change, non-uniform integration time and integrator transient effects.
2. The phototube, crystal and high voltage supply.
3. The americium source.
4. Removal and replacement of a sample cell.

The phototube was disconnected from the lower integrator and a constant current source was connected to this integrator input. The timer was run through its cycle several times and (V_P) and (V_S) were recorded. The ratios (V_P/V_S) were then computed. The standard deviation of these ratios amounted to 0·01% of the (V_P/V_S) ratio which gives an estimate of the variability of the first component.

The source as a long-lived radionuclide has Poisson statistics. The variability in this component may be directly calculated from the source intensity, the geometry, the reference cell attenuation and the NaI crystal efficiency. Such a calculation gives an effective intensity of $1{\cdot}5 \times 10^7$ γ/min at the phototube with a standard error of 0·026%.

A comparison of sample cell analysis where the sample cell was left in place for varying numbers of analyses and where it was removed and replaced in the normal manner showed there was no detectable positioning effect, transient effect, or effect from phototube hysteresis.

No method was readily available to determine the variability of the phototube-crystal-high voltage supply component. However, it appears, by process of elimination, that the major part of the random noise in the absorptiometer calibration must be attributed to random short term fluctuations in the phototube-crystal system sensitivity or to possible high voltage fluctuations of a magnitude greater than the 1 part in 10^5 quoted by the manufacturer.

CONCLUSIONS

The data-logging absorptiometer described in this paper has been in operation for approximately two years. About 2000 samples have been analysed during this time. An average of 30 samples/8-hr day has been achieved by the laboratory using the apparatus and very few operator errors have been made. When an error has occurred, it has been gross and easily detected. An incorrect setting of the cell-size switch has been the most frequent error. Here, the data point is still salvable by adjusting the data for the capacitance change. The goal of a rapid, foolproof and accurate method of uranium analysis has thus been achieved.

The method developed to calibrate the absorptiometer for organic phase solutions is original with this paper. The method clearly eliminates the necessity of preparing organic phase standards which is, in general, difficult.

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Inclusion of the scattering term in the section *Mathematical model of absorption*, which greatly improves the model, was suggested by A. Whittaker.

Zusammenfassung—Urankonzentrationen in wäßrigen und organischen Lösungen werden durch Gamma-Absorptionsmessung bestimmt. Eine ^{241}Am-Quelle, die 60 keV-Quanten emittiert, und ein Szintillationsdetektor werden verwendet. Der von der Photozelle gelieferte Strom wird über eine Minute integriert und liefert ein 2–10 V Gleichstromsignal, das in einer Datenspeicheranlage registriert wird. Mit einer einzigen Methode, die nur wäßrige Standards erfordert, wird das System für wäßrige und organische Uranlösungen geeicht. Eine eingehende statistische Analyse der Versuchsergebnisse ist beigefügt. Eine Abweichung vom Beerschen Gesetz wird durch die Berücksichtigung von Streueffekten im Modell erklärt. Lösungsanalysen mit dieser Anlage sind genauer als ±0,5 g/l bei Urankonzentrationen von 0–120 g/l.

Résumé—Les concentrations en uranium de solutions aqueuses et organiques sont déterminées par absorptiométrie gamma. On utilise une source de ^{241}Am qui émet des photons d'énergie 60 keV, et un détecteur à scintillation. Le courant de sortie du phototube est intégré pendant 1 min, donnant un signal de 2–10 V en courant continu, qui est noté par un système enregistreur. Pour étalonner le système on utilise, tant pour les solutions aqueuses que pour les solutions organiques d'uranium, une méthode unique ne nécessitant que des étalons aqueux. Une analyse statistique détaillée des résultats expérimentaux est incluse. On explique une déviation notée par rapport à la loi de Beer par la présence d'effets de dispersion dans le modèle décrit. Les analyses de solutions faites avec ce modèle donnent des résultats d'une précision supérieure à ±0,5 g/l, pour des concentrations en uranium comprises entre 0 et 120 g/l.

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MUTUAL RADIATION INTERFERENCE EFFECTS OF THE ALKALI ELEMENTS AND HYDROGEN UPON THE RESONANCE LINE INTENSITIES OF THE ALKALI ELEMENTS IN FLAME SPECTROPHOTOMETRY*

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Summary—The mutual interference effects of different concentrations of each of the alkali elements and hydrogen, as the chlorides in solution, on the intensity of the resonance line for four different concentrations of each of the alkali elements have been studied. All concentrations have been expressed in millimoles per litre. The interference effects were greatest on the lowest concentration and least on the greatest concentration of each element. In general, lithium produced the least effect on the other elements, and the other elements had the least effect on lithium. Hydrogen ion, as hydrochloric acid, caused suppression because of the anion effect, with caesium being suppressed the most. Caesium and rubidium caused the greatest enhancement on the other elements. Because of their very low ionisation potentials, the mutual interference effects of rubidium and caesium on each other were found to be very large.

INTRODUCTION

THIS work, which was started several years ago, was designed to be a careful study of the interference effects for a broad concentration range of the alkali chlorides and hydrochloric acid upon the resonance line radiation of each of the alkali elements. Many brief studies on "interferences", usually associated with a procedural development and with limited concentration ranges, have been performed for lithium, sodium and potassium. In comparison, relatively few studies are available for rubidium and caesium. However, it is difficult to evaluate much of the results reported in the literature, because the work was performed with different types of instrument, different types of burner and fuel, and under different and sometimes unstated operating conditions. Very often, insufficient attention was given to such problems as purity of reagents, sources and degree of contamination, and care in the preparation of the solutions. The authors found rubidium and caesium salts from most sources to contain high concentrations of the other element, as well as of potassium. Work done with impure solutions, as indicated above, cannot yield reliable results. Much of the information in the literature is not in agreement, and there are often examples of conflict. For example, sodium and potassium have been reported to suppress[2] and to enhance[24] their respective emission intensity. It has also been reported that excess sodium caused both high and low results for potassium, depending on the potassium

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concentration,[3] and only high results for different potassium concentrations.[19] Higher concentrations of hydrogen chloride have been reported to enhance[21] and to suppress the emission of the lithium 671-mμ line.[16] It has also been reported that these effects were not observed when an optical system of adequate resolving power was used.[17]

This study represents an effort to obtain more reliable interference effects results with respect to the elements of Group I of the Periodic Table, and to examine further some of the factors that effect the equilibrium constant expression:

$$K = \frac{[M^+][e^-]}{[M]} = \frac{[x^2]}{[1 - x]} P \tag{1}$$

when x = degree of ionisation of the metal atoms,
and P = partial pressure for each species in the flame.
The above may also be expressed directly in terms of the partial pressure equilibrium constant

$$K_P = \frac{[P_M{}^+][P_e{}^-]}{[P_M]} \tag{2}$$

Although this paper represents results from a large number of solutions with different concentrations, this and other published results do not appear to be sufficiently quantitative to be reduced to a common correction factor, because there are numerous factors that can effect the partial pressure of the atomic species in the flame. However, because of the range of concentrations examined, the results will serve as a guide to the spectrochemist on the magnitude of the interferences that may be expected.

The present study involved only aqueous solutions, the integral aspirator burner, and the use of oxygen-hydrogen fuel.

EXPERIMENTAL

Equipment and materials

Beckman model DU spectrophotometer equipped with the 9200 flame attachment, oxygen-hydrogen burner, 9200 spectral energy recording attachment, and a Brown electronic recorder with a 0- to 10-mV scale and a ½-second pen response.

Borosilicate glassware was used for all volumetric measurements but not for the storage of any solutions. All volumetric ware used in this study met the requirements as specified in N.B.S. Circular 602 and Federal Specifications DD-V-581a.

Standard platinum tips or *No. 27 hypodermic syringe needles* were used with the 5-ml (sub-divisions, 1/100 ml) semimicro burettes.

Polyethylene bottles were used as containers. These bottles were steamed, then leached with ion-exchange water before they were used. Water stored in these bottles did not show the changes observed by Delhez.[7] When the solutions were stored for a few weeks or longer for future reference, the bottles were sealed with tape, because for small polyethylene bottles a cap screwed on tightly does not necessarily assure a sealed bottle.

All the *alkali chlorides* used in this work were Johnson, Matthey Specpure grade. The *hydrochloric acid* was redistilled. All solutions were prepared with ion-exchange water that had been previously distilled, then passed through a column containing no metal or rubber parts. Attempts were made to use some standard A.C.S.-grade chemicals for some of the solution concentrations. However, these were found to be quite unsatisfactory because of traces of impurities of the analyte, and so were replaced with solutions prepared from Specpure chemicals.

Procedure and precautions

Solutions. Four concentrations of each element; namely, 0·375, 0·75, 1·5 and 3·0 millimoles per litre, were studied in order to cover the usual concentrations that may be found in analytical work. The concentration of the added mutually interfering cations was varied from 0 to 2000 millimoles per litre for the alkali salts and from 0 to 5000 millimoles per litre for the acid. These units of concentration were used instead of parts per million, in order to have all solutions in the same concentration ratios. In addition to the stock solutions, 1340 separate sample solutions were required.

In case of questionable results all the solutions for a series of a given concentration, such as 0·375 millimoles per litre of caesium, were reprepared. To avoid other anion influences, chlorides were used for all solutions.

Testing for impurities. All water used was from an ion-exchange column containing no metal parts and charged with the mixed-bed resin Amberlite IR 400. All water, glassware, polyethyleneware, and stock solutions were checked for contamination before use by looking for the resonance line of each of the alkali elements. This was done by aspirating the water or solution in question into the flame and recording the response for the resonance line of the possible contaminating element. If no response was obtained, the items were considered to be satisfactory.

A series of solutions with concentrations from 0 to 2000 millimoles per litre for each alkali element were prepared from the stock solutions to serve as blanks. Each concentration of the series was checked by scanning the resonance line for each analyte under the same operating conditions as those in which the line intensity of that analyte was determined. These served as an additional check for contamination, as well as for possible line and background interferences.

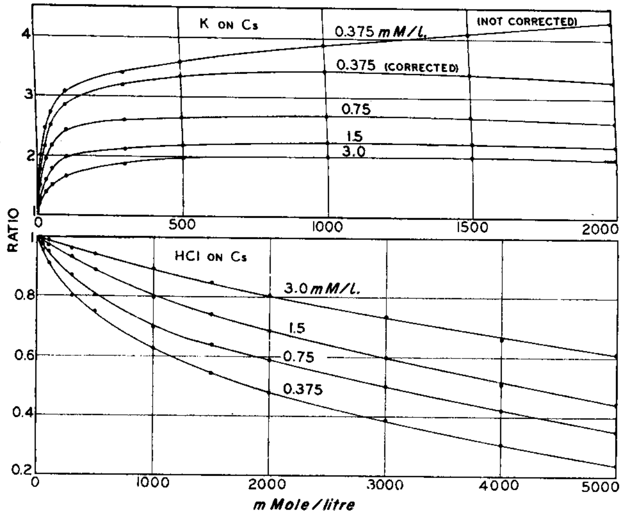

FIG. 1.—Example of mutual interference as a function of concentration of analyte.

If a very small amount of the analyte is present as an impurity in the interferent, or if weak lines of the interferent are closely adjacent to the resonant line of the analyte, it is readily detected in the results unless corrections are made for background and weak-line interferences. This is illustrated in Fig. 1 for the effect of potassium on the concentration 0·375 millimole of caesium per litre. The top curve, uncorrected, shows the effect of a possible minute trace of caesium in the potassium salt which is being added to the caesium solution, and increasing background as the concentration was increased. By spectrographic examination, traces of caesium have been observed in some samples of commercial A.C.S.-grade potassium chloride, but not in others.

The second curve shows the effect of potassium corrected for background interference at 8521·1 A from the potassium chloride solutions. It is doubtful whether the very weak potassium doublet 8503·8 and 8505·2 A produced any influence, because these lines were not observed on sensitive infrared emulsion when potassium chloride was burned in a low current d.c. arc or when a 1*M* potassium chloride solution was aspirated into an oxygen-hydrogen flame for as long as 2 hr.

Ratio of intensities. The samples were aspirated into the flame, and the resulting intensities were recorded on the strip-chart recorder. A pure solution was burned with each solution containing a given concentration of the mutually interfering element, in order to compare the intensities for the pure sample and the sample containing the interfering element. Two or three runs were made on each sample-reference pair at different times, and the intensities were calculated in terms of the ratio:[12]

$$R = \frac{I_{\text{analyte+interferent}}}{I_{\text{analyte}}} \tag{3}$$

By this method it was possible to detect drift or any unusual equipment variation, and to compensate for minor variations, such as slow drift or small variations in instrument settings. The values of R greater than 1 indicate enhancement and those less than 1 indicate suppression of the intensities of the resonance lines for the elements.

The slit widths were adjusted to obtain approximately 0·3–0·4 full-scale responses for each element at each concentration. Changes were made when the enhancement or suppression became very large.

DISCUSSION

The mutual radiation interferences on each of the alkali elements were studied in four concentrations, 0·375, 0·75, 1·5 and 3·0 millimoles per litre. Contamination effects, effects arising from line and band overlapping, and background interferences were examined, and compensations were made on the graphs.

The mutual radiation interference effects of the acid and the other alkali elements on each individual alkali element are summarised in Figs. 1–4 and are tabulated in Table I. At the low concentrations, these results are in general agreement with those listed by Dean.[6] A given concentration of the interfering element has the least enhancement or suppression effect on the most concentrated solutions of the same analyte. This is illustrated in Fig. 1 by the effects of potassium and hydrogen chloride on the four concentrations of caesium. The concentration 1000 mmole/l. of potassium caused a radiation enhancement on the 3·0-mmole/l. concentration of caesium by a factor of 2, and the 0·375-mmole/l. concentration was enhanced by a factor of 3·4. The $2M$ acid concentration caused twice as much suppression of the 0·75-mmole/l. concentration of caesium as of the 3·0-mmole/l. concentration.

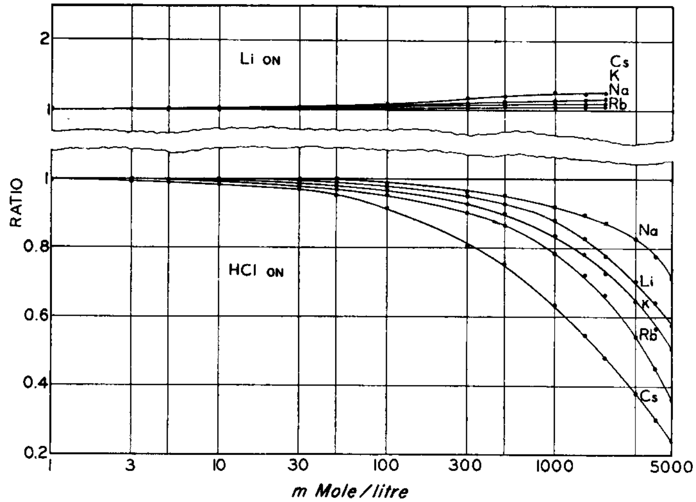

FIG. 2.—Mutual interference effect of lithium and hydrochloric acid.

In order to discuss the experimental results in Figs. 1–4 and Table I, the following equilibrium reactions must be considered, because these are involved in the reactions in the flame and affect the intensities of the resonance lines.

$$M \leftrightharpoons M^{+} + e \tag{4}$$

$$M + OH \leftrightharpoons MOH \tag{5}$$

$$M + Cl \leftrightharpoons MCl \tag{6}$$

$$H + Cl \leftrightharpoons HCl \tag{7}$$

$$H + OH \leftrightharpoons HOH \tag{8}$$

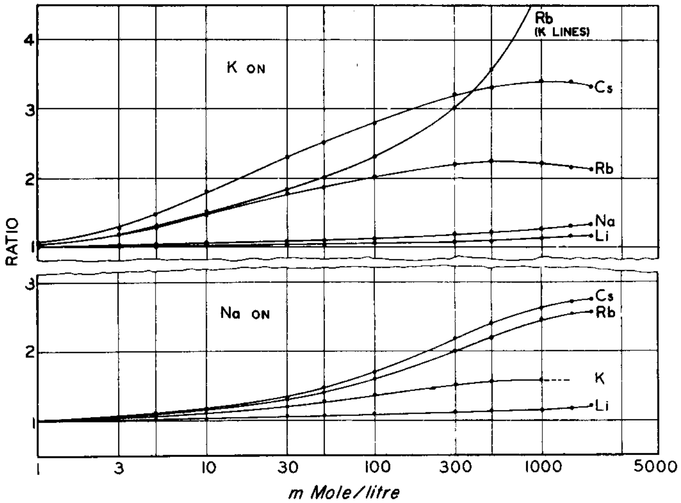

FIG. 3.—Mutual interference effect of potassium and sodium.

Although these probably do not exist in a true equilibrium in the usual chemical sense, a steady state of balanced dissociation and recombination does exist. Thus, from the equilibrium constant values, dissociation energies and other physical constants, the effect of the competing reactions on the resonance line intensities can be estimated. Unfortunately, reliable values are still not available in the literature.

The suppression effect of the aqueous hydrogen chloride results from the formation of the relatively stable chloride,[5,18] the reaction following the mass action law,

$$\frac{[P_M][P_{Cl}]}{[P_{MCl}]} = K_P \tag{9}$$

that reduces the number of free atoms available for excitation.

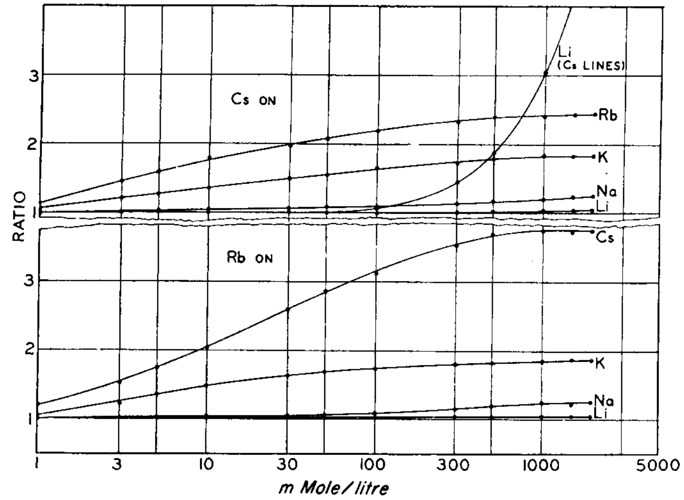

FIG. 4.—Mutual interference effect of caesium and rubidium.

TABLE I.—CHANGES IN EMISSION INTENSITY BECAUSE OF INTERFERENCE EFFECTS

Interferent	Concentration		Change in emission intensity, %				
			Analyte	Concentration			
	mm/l.	*ppm*	Na	0·375	0·75	1·5	3·0 *mm/l.*
Li				8·6	17·2	34·5	69·0 *ppm*
	1	6·94		0	0	0	0
	3	20·8		0	0	0	0
	5	34·7		0	0	0	0
	10	69·4		0·5	1	0	0
	30	208		2	1	0	0
	50	347		2	2	1	−0·5
	100	694		3	2	1	−0·5
	300	2082		6	3·5	2	0
	500	3470		7	5	2	1
	1000	6940		9·5	6	3	1
			(Slit width	0·10	0·08	0·05	0·045 *mm*)
Li			K	14·7	29·3	58·6	117·3 *ppm*
	1			0	0	0	0
	3			0	0	0	−1
	5			1	0	0	0
	10			1·5	0	0	0
	30			3	1	0	0
	50			3·5	2	0	0
	100			5	3	1	0
	300			8	5	3	1
	500			9·5	6	3	2
	1000			12	7	4	2
			(Slit width	0·05	0·04	0·04	0·03 *mm*)
Li			Rb	32·0	64·1	128·2	256·4 *ppm*
	1			0	0	0	0
	3			0	0	0	−1
	5			0	0	0	−1
	10			0	0	0	−1
	30			0	0	−1	−1
	50			1	0	−1·5	−2
	100			2	1	−1	−2
	300			3	1·5	−1·5	−3
	500			4	1·5	−1	−3
	1000			5	1	−1	−5
			(Slit width	0·055	0·045	0·035	0·03 *mm*)
Li			Cs	49·8	99·7	194·4	398·8 *ppm*
	1			0	0	0	0
	3			0	0	0	0
	5			−0·5	−0·5	−0·5	0
	10			1	−1	−1	−1
	30			2	−1	−1	−2
	50			3	−1	−1	−2·5
	100			6	1	−1	−2·5
	300			16	5	−1·5	−3
	500			19	6·5	−3	−3·5
	1000			24	9	−4	−5·5
			(Slit width	0·07	0·05	0·04	0·03 *mm*)

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %				
			Analyte	Concentration			
	mm/l.	*ppm*	Li	0·375	0·75	1·5	3·0 *mm/l.*
Na				2·6	5·2	10·4	20·8 *ppm*
	1	23·0		0	0	0	−1
	3	69·0		1	1	1	0·5
	5	115		2·5	2·5	2·5	2
	10	230		4	3	2	2
	30	690		6	5	4	3
	50	1150		8	7	4	3
	100	2299		10	10	6	5
	300	6897		12	10	9	8
	500	11,496		16	12	11	10
			(Slit width	0·1	0·1	0·08	0·06 *mm*)
Na			K	14·7	29·3	58·6	117·3 *ppm*
	1			1	0·5	0	0
	3			4	2·5	1	0
	5			6	4	3·5	1
	10			12	6	4	2
	30			22	13	8	5
	50			30	19	12	8
	100			36	21	13	10
	300			50	32	20	14
	500			55	35	23	17
			(Slit width	0·05	0·04	0·04	0·03 *mm*)
Na			Rb	32·0	64·1	128·2	256·4 *ppm*
	1			2	1	0	0
	3			5	3	1	2
	5			10	5	3	2·5
	10			15	9·5	6·5	5
	30			30	23	16	10
	50			46	33	22	14
	100			70	51	34	20
	300			100	74	54	40
	500			121	87	65	45
			(Slit width	0·055	0·045	0·035	0·03 *mm*)
Na			Cs	49·8	99·7	199·4	398·7 *ppm*
	1			2	1	1	0
	3			6	4	2	2
	5			11	7	4	2
	10			18	14	7	5
	30			42	34	20	11
	50			56	48	26	14
	100			78	70	40	25
	300			120	111	74	38
	500			140	129	87	48
			(Slit width	0·07	0·05	0·04	0·03 *mm*)

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %						
			Analyte	Concentration					
	mm/l.	*ppm*	Li	0·375		0·75	1·5	3·0 *mm/l.*	
K				2·6		5·2	10·4	20·8 *ppm*	
	1	39·1		0·5	1*	0·5	0	0	
	3	117		0·6	1	0·5	0·5	0	
	5	196		1	4·5	1	1	1	
	10	391		2	8	1	1·5	1	
	30	1,173		4·5	10	2·5	2·5	1	
	50	1,955		5·5	16	3	3	2	
	100	3,910		6	22	3	3	2	
	300	11,730		6	40	4	3·5	3	
	500	19,100		8	60	5	3·5	3	
			(Slit width	0·10		0·10	0·08	0·06 *mm*)	
K			Na	8·6		17·2	34·5	69·0 *ppm*	
	1			1		1	0	0	
	3			2		1·5	1	0	
	5			3		2·5	2	0·5	
	10			5		3·5	3	1	
	30			8·5		6	4·5	2·5	
	50			10		7·5	5·5	4	
	100			12·5		9·5	7	4·5	
	300			17		14	10	6	
	500			20		16	12	8	
			(Slit width	0·10		0·08	0·05	0·045 *mm*)	
K			Rb	32·0		64·1	128·2	256·4 *ppm*	
	1			5	6*	4	3	1	2*
	3			15	16	10	10	3	4
	5			27	30	22	16	6	8
	10			48	52	38	26	12	14
	30			77	84	60	44	26	30
	50			87	100	72	54	32	38
	100			98	130	82	68	40	50
	300			120	200	102	80	53	70
	500			124	355	108	84	64	85
			(Slit width	0·045		0·035	0·03	0·03 *mm*)	
K			Cs	49·8		99·7	199·4	398·7 *ppm*	
	1			10	15*	10	6	3·5	
	3			27	45	23	19	9	
	5			45	75	37	22	11	
	10			81	104	58	37	22	
	30			130	151	93	62	40	
	50			152	173	115	78	51	
	100			178	208	142	97	66	
	300			220	240	160	110	85	
	500			230	260	165	118	99	
			(Slit width	0·05		0·04	0·03	0·025 *mm*)	

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %				
			Analyte	Concentration			
	mm/l.	*ppm*					
Rb			Li	0·375	0·75	1·5	3·0 *mm/l.*
				2·6	5·2	10·4	20·8 *ppm*
	1	85·5		0	−1	−0·5	−0·5
	3	256·4		1	0	−1	−1
	5	427·4		2	0	−1	−0·5
	10	854·8		2	0	0	0
	30	2,564		3	0	0	0
	50	4,274		3	1	1	0
	100	8,548		4	1	1	1
	300	25,644		4	2	1	1·5
	500	42,740		4	3	1	3
			(Slit width	0·10	0·10	0·08	0·06 *mm*)
Rb			Na	8·6	17·2	34·5	69·0 *ppm*
	1			1	1	0	0
	3			2	1·5	1	1
	5			3·5	2·5	2	2
	10			4	4	2·5	2·5
	30			5·5	4·5	4	2·5
	50			7·5	6	5	3·5
	100			10	7·5	6	5
	300			14	11	9	6
	500			16	13	11	8
			(Slit width	0·10	0·08	0·05	0·045 *mm*)
Rb			K	14·7	29·3	58·6	117·3 *ppm*
	1			6	4	2	1
	3			24	13	10	5
	5			38	24	15	9
	10			50	33	19	13
	30			62	44	24	16
	50			66	46	30	19
	100			72	53	34	22
	300			79	58	37	25
	500			81	63	39	25
			(Slit width	0·045	0·04	0·03	0·025 *mm*)
Rb			Cs	49·8	99·7	199·4	398·7 *ppm*
	1			26	20	11	5
	3			55	47	26	13
	5			73	61	39	19
	10			108	91	56	34
	30			160	120	101	54
	50			188	143	116	60
	100			209	165	132	80
	300			252	188	150	93
	500			270	201	159	96
			(Slit width	0·05	0·04	0·03	0·025 *mm*)

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %				
			Analyte	Concentration			
	mm/l.	*ppm*	Li	0·375	0·75	1·5	3·0 *mm/l.*
Cs				2·6	5·2	10·4	20·8 *ppm*
	1	132·9		0	0	0	0
	3	398·7		0	0	0	0
	5	664·6		0	0	0	0
	10	1,329		0	0	0	0
	30	3,987		1	0	0	1
	50	6,646		2 5*	0 4*	1 3*	1 1·5*
	100	13,291		2 11	0 8	1 7	1 4
	300	39,873		3 44	1 37	2 20	2 6
	500	66,455		3 87	2 76	2 39	2 12
			(Slit width	0·10	0·08	0·07	0·06 *mm*)
Cs			Na	8·6	17·2	34·5	69·0 *ppm*
	1			1	1	0	0
	3			3	2·5	1	1
	5			4·5	3	2	1
	10			7	5	2·5	1·5
	30			8	6	3·5	2·5
	50			9	6	4	3
	100			12	8	5·5	4·5
	300			15	10	7·5	5·5
	500			17	11·5	9	6·5
			(Slit width	0·10	0·08	0·05	0·045 *mm*)
Cs			K	14·7	29·3	58·6	117·3 *ppm*
	1			8	5	4	2
	3			21	18	12	6
	5			28	24	14	10
	10			38	31	22	13
	30			49	42	33	26
	50			58	46	37	28
	100			70	54	42	35
	300			76	66	49	43
	500			82	70	54	47
			(Slit width	0·045	0·04	0·03	0·025 *mm*)
Cs			Rb	32·0	64·1	128·2	256·4 *ppm*
	1			16	10	6	4
	3			46	29	22	14
	5			57	38	34	18
	10			80	55	45	26
	30			98	68	56	40
	50			106	82	70	47
	100			120	90	82	56
	300			134	98	90	63
	500			139	101	93	70
			(Slit width	0·045	0·035	0·03	0·025 *mm*)

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %				
	mm/l.	*ppm*	Analyte	Concentration			
			Li	0·375	0·75	1·5	3·0 *mm/l.*
HCl				2·6	5·2	10·4	20·8 *ppm*
	1			0	0	0	0
	3			0	0	0	0
	5			0	0	0	0
	10			0	0	0	0
	30			0	−0·5	0	0
	50			−1	−1	−1	−0·5
	100			−2·5	−2·5	−1·5	−1·5
	300			−6	−4·5	−4·0	−4
	500			−8	−7·5	−6·5	−5·5
	1000			−13·5	−12·5	−12·5	−10·5
			(Slit width	0·10	0·10	0·08	0·08 *mm*)
HCl			Na	8·6	17·2	34·5	69·0 *ppm*
	1			0	0	0	0
	3			0	0	0	−0·5
	5			0	0	0	0
	10			0	0	0	0
	30			0	0	0	0
	50			−0·5	0	−0·5	0
	100			−1	−0·5	−0·5	0
	300			−3	−2	−1	0
	500			−5	−3	−1·5	−1
	1000			−9	−4·5	−3·5	−2·5
			(Slit width	0·10	0·08	0·06	0·06 *mm*)
HCl			K	14·7	29·3	58·6	117·3 *ppm*
	1			0	0	1	1
	3			0	0	1	1
	5			0	0	0	0·5
	10			0	0	0	0
	30			−1	−0·5	0	0
	50			−2	−1	−1	0
	100			−4	−3	−1·5	−1
	300			−7	−5·5	−3·5	−2·5
	500			−10	−8	−6	−3·5
	1000			−18	−13·5	−9	−7
			(Slit width	0·045	0·045	0·035	0·035 *mm*)
HCl			Rb	32·0	64·1	128·2	256·4 *ppm*
	1			0	0	0	0
	3			0	0	0	0
	5			0	0	0	0
	10			−1	0	0	0
	30			−2	−1	−0·5	0
	50			−3	−2	−1	0
	100			−5	−3	−2	−1
	300			−11	−7	−5	−2·5
	500			−15	−10	−7	−4
	1000			−23	−17	−13	−7·5
			(Slit width	0·04	0·04	0·04	0·04 *mm*)

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %				
			Analyte	Concentration			
	mm/l.	*ppm*	Cs	0·375	0·75	1·5	3·0 *mm/l.*
HCl				49·8	99·7	199·4	398·7 *ppm*
	1			0	0	0	0
	3			−1	0	0	0
	5			−1	0	0	0
	10			−2	−1·5	−1	0
	30			−3	−2	−1	−0·5
	50			−4·5	−3	−1	−0·5
	100			−9	−5	−2·5	−1
	300			−20	−13	−6·5	−4
	500			−25	−20	−11	−6
	1000			−37·5	−30·5	−20·5	−10
			(Slit width	0·05	0·05	0·05	0·05 *mm*)

* Not corrected for background and other interferences; integral aspirator burner; oxygen, 2·6 l./min; hydrogen, 5·6 l./min.

The greatest suppression of resonance line radiation (Fig. 1) is on the lowest concentration of analyte, because at a given concentration of interferent its mass action effect is greater on the available analyte atoms, thus making a greater proportion unavailable for excitation.

The degree of suppression for each of the alkali elements in the presence of hydrochloric acid is illustrated in Fig. 2. Anion effects of both the chloride and the hydroxide are involved. At the low concentrations of hydrogen chloride the ratio M:MOH and Cl:HCl will largely be fixed, because of the high concentration of the OH and H in the flame. With an increase in the hydrogen chloride aspirated into the flame, and the resulting greater concentration of chloride, there is a shift in the metal atom-metal chloride equilibrium accompanied by a decrease in the M:MCl ratio [equation (6)] and a proportional decrease in the intensity of the resonance line radiation. The increasing suppression of the potassium, rubidium and caesium resonance line radiations is a result of the formation of the increasingly stable metal chlorides, with caesium chloride having the highest dissociation energy.

If the formation of the non-dissociated alkali-metal hydroxides is not considered, this is in agreement with the dissociation energies as determined by Bulewicz *et al.*,[4] but not in agreement with the values determined by Somayajulu[22] for caesium and rubidium chloride (Table II). Dissociation energies for the alkali-metal hydroxides are not available. However, based on the deviation of the degree of ionisation as predicted from the Saha equation[23] and a study of hydroxide formation,[14] the stability of the gaseous alkali-metal hydroxides is in the order $\mathrm{Na} < \mathrm{K} < \mathrm{Rb} < \mathrm{Cs} < \mathrm{Li}$. Lithium forms a very stable gaseous hydroxide. There was no deviation for sodium, so the gaseous sodium hydroxide is so unstable as to be effectively absent in the flame. The gaseous potassium hydroxide is nearly as unstable as the sodium hydroxide, and the rubidium and caesium hydroxides are progressively a little more stable.

In addition, the MOH:M ratios,[13] of Table II, would indicate that the formation of potassium, rubidium and caesium hydroxide molecules had no effect or only a minor effect on the resonance line radiation-suppression for these elements. The sodium resonance line radiation was suppressed the least, because sodium hydroxide essentially does not exist in the flame and the sodium chloride has the lowest dissociation energy.

The suppression effect of hydrogen chloride on the intensity of the lithium resonance line is only a little greater than that for sodium. Lithium chloride has the greatest dissociation energy (Table II), and the hydrogen chloride should have a similar mass action effect to form lithium chloride as the other alkali chlorides, if the formation of the stable lithium hydroxide could be neglected. This would indicate that the lithium already exists largely as the highly stable lithium hydroxide, and that few lithium atoms are available to form the stable lithium chloride molecule, thus only a small suppression was observed. If the lithium hydroxide were largely dissociated, then there would be a large suppression arising from the mass action effect of the excess hydrogen chloride and the high dissociation energy of the lithium chloride molecule.

TABLE II.—PHYSICAL VALUES FOR GROUP I ELEMENTS

Element	Resonance line, *A*	Excitation potential, *eV*	Ionisation potential, *eV*	* Ionisation in the flame, %[9]		
				Air-propane (2200°K)	H_2—O_2 (2450°K)	C_2H_4—O_2 (2800°K)
Li	6707·8	1·84	5·39	0·01	0·9	16·1
Na	5890·0	2·10	5·14	0·3	5·0	26·4
	5895·9	2·10				
K	7664·9	1·61	4·34	2·5	31·9	82·1
Rb	7800·2	1·56	4·18	13·5	44·4	89·6
Cs	8521·1	1·39	3·89	28·3	69·6	96·4

Chloride	Dissociation energy				$\frac{\text{MOH}}{\text{M}}$ Ratio[13]
	Bulewicz *et al.*[4]	Somayajulu[22]	Gaydon[10]		
Li	110·5 ± 3 *kcal.*	4·8 eV.	5·0 ± 0·3 *kcal.*	115 eV.	4·4
Na	97·5 ± 2	4·12	4·24 ± 0·05	97·6	0
K	99·6 ± 2	4·32	4·40 ± 0·05	101·4	0·19
Rb	101·5 ± 2	4·76	4·5 ± 0·2	103	0
Cs	107·2 ± 3	4·38	4·6 ± 0·2	106	0·37

* Based on a partial pressure of 10^{-6} atmos for the metal atoms in the flame.

The addition of a second ionisable substance, interferent, causes an increase in the partial pressure of the free electrons in the flame. This, through the mass action effect, will decrease the M^+: M ratio in the analyte and increase the population of neutral atoms available for excitation. The partial pressure of the free electrons depends on the ionisation potential and concentration of the interferent. In addition the decrease in the ratio of M^+: M is also dependent on the ionisation potential and concentration of the analyte.

Thus, if the ionisation potential of the analyte is high, there will be few ions from any given concentration, so that even though a relatively large population of electrons is supplied from an interferent, the observed enhancement will be small. This is illustrated by the effect of the other alkali elements on lithium (Figs. 3 and 4).

If the ionisation potential of the analyte is low, a relatively large percentage of the atoms will be ionised, so that an appreciable increase in the electron population from the interferent will cause a large mass action effect, and the observed degree of enhancement will be large. This is most strikingly illustrated by the enhancement effect of caesium on rubidium, and rubidium on caesium (Fig. 4). The degree of enhancement will be greatest on the lowest concentration of analyte, as illustrated by the effect of potassium on different concentrations of caesium (Fig. 1), because the mass action effect of the electron population is greater on the analyte ions, thus making a greater proportion of the atoms available for excitation. In addition, a greater degree of ionisation would have taken place at the lower concentrations.

Caesium, with its low excitation potential (3·89 eV) is highly ionised in the oxygen-hydrogen flame (Table II). The relatively high concentration of electrons causes an appreciable decrease in the $M^+:M$ ratio of the analyte. The degree of this change is dependent on the M^+ population of the analyte, which in turn is dependent on its ionisation potential. Thus, at a given concentration of the analyte, a given concentration of caesium has the greatest enhancement on rubidium (excitation potential 4·18 eV), and successively lesser effect on potassium (4·34 eV), sodium (5·14 eV) and lithium (5·39 eV) (Fig. 4). A similar relation is shown for the effect of rubidium on potassium, sodium and lithium, and of potassium on sodium and lithium. This was also observed for caesium and rubidium on the other alkali elements by Farquhar and Hill[8] and by Bernstein.[1]

In the case of two interferents at a given concentration, the interferent with the lowest ionisation potential may be expected to have the greatest enhancement effect on the analytes with higher excitation potentials. Thus, the enhancement effect caused by caesium on the other alkali elements with higher ionisation potentials should be greater than that caused by rubidium, assuming no other factors to be present. These differences were generally observed (Fig. 4, Table I), although they were not always large.

An interferent with a relatively high ionisation potential, such as sodium, will have the greatest enhancement effect on the resonance line radiation of the analyte with the lowest ionisation potential. Although the additional electron population produced by the interferent is not great, its mass action effect and subsequent enhancement will be greater on the analyte which is ionised to the greatest degree in the flame. This is illustrated by the greater enhancement effect of sodium and of potassium on caesium than on rubidium (Fig. 3). This greater enhancement of an analyte with the lowest excitation potential is illustrated by the results showing that the enhancement effect of rubidium on caesium is greater than that of caesium on rubidium; the effect of potassium is greater on rubidium than that of rubidium on potassium; and the effect of sodium is greater on potassium than that of potassium on sodium (Fig. 3 and 4). The enhancement effects of caesium on rubidium and of rubidium on caesium are somewhat greater than those reported in the more limited results by Pro *et al.*[20]

The presence of lithium causes very little radiation effect on the other alkali elements (Fig. 2). In addition, the radiation intensity of its resonance line is least affected by the presence of the other alkali elements. This would be a result of its high ionisation potential (5·37 eV), so that only a very small percentage of the total atom population is ionised, and any mass action effect is very small. It is suggested that the gaseous lithium hydroxide is quite extensively dissociated in the oxygen-hydrogen flame,[11] so that the small mutual radiation effect of lithium on the other elements is a consequence of its high ionisation potential and not because of its hydroxide making atoms unavailable for ionisation.

The effect of caesium on lithium (Fig. 4) results from the relatively weak caesium 6723·3 A line-addition effect on the lithium 6707·8 A line. Recording of caesium radiation in this region indicated the presence of this line but no band structures.

The large enhancement of potassium on rubidium (Fig. 3) results from spectral interferences of the strong potassium 7699·0 A line, and at very high concentrations the 7664·9 A and 7699·0 A doublet. Part of this error was thought to result from the presence of the K_2 band in this spectral region.[15] However, a brief study using a spectrograph with a large reciprocal dispersion did not reveal these bands in any part of the flame. The true enhancement of rubidium is lower than would be expected (Fig. 3), considering the enhancement of sodium on rubidium and the excitation potential values (Table II). This may be the result of subtracting an incorrect value for the blank, because the rubidium line appears on the shoulder of the spectral tracing for the potassium line.

The temperature also influences the degree of the mutual-cation-enhancement effect. In a hot flame the degree of ionisation of an easily ionised analyte is large (Table II). A high concentration of electrons from an interferent will have a large mass action effect, so that the relative enhancement will be large. If the degree of ionisation of the analyte and interferent is less, as in a lower temperature flame, the degree of enhancement will be less.

Zusammenfassung—Die gegenseitigen Störeinflüsse verschiedener Konzentrationen aller Alkalien und Wasserstoff, die sich als Chloride in der Lösung befanden, auf die Intensität der Resonanzlinie wurden für vier verschiedene Konzentrationen aller Alkalien untersucht. Alle Konzentrationen wurden in Millimolen pro Liter ausgedrückt. Die Störungen waren am größten bei der geringsten und am kleinsten bei der höchsten Konzentrationen jedes Elements. Allgemein beeinflußte Lithium die anderen Elemente am wenigsten und andere Elemente das Lithium am wenigsten. Salzsäure bewirkte wegen des Anioneffekts Verringerung, am meisten beim Caesium. Caesium und Rubidium rufen die größte Erhöhung bei den anderen Elementen hervor. Wegen ihrer sehr niedrigen Ionisationspotentiale stören sich Rubidium und Caesium gegenseitig sehr stark.

Résumé—Les effets de l'influence mutuelle des diverses concentrations des éléments alcalins et de l'hydrogène comme les chlorures en solution, sur les intensités des raies de raisonnance pour quatre concentrations de chacun des éléments alcalins ont été étudiés. Toutes les concentrations sont exprimées en millimoles par litre. Les effets de cette interférence se manifestent le plus aux plus faibles concentrations et réciproquement. En général, le lithium produit le plus faible effet sur les autres éléments, et les autres éléments ont le moins d'effet sur le lithium. L'hydrogène, comme l'acide chlorhydrique, supprime cet effet par action de l'anion, principalement sur le césium. Le césium et le rubidium exercent la plus grande exaltation sur les autres éléments. A cause de leurs potentiels d'ionisation très bas, les effets d'interférence mutuelle du rubidium et du césium sont très importants.

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SPECTROPHOTOMETRIC DETERMINATION OF RHENIUM(VII) AFTER EXTRACTION WITH 2-THENOYLTRIFLUORACETONE

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Summary—A new method is proposed for the determination of rhenium(VII) at the microgram level. 2-Thenoyltrifluoracetone in isoamyl alcohol-benzene extracts rhenium(VII) quantitatively from 7–9N sulphuric acid. Treatment of this organic extract with tin(II) chloride and potassium thiocyanate gives a yellow coloured product which can be measured at 430 mμ. Beer's law is valid over the concentration range of 0·5–5 μg of rhenium/ml. The effect of diverse ions has been studied.

THE well-known chelating agent 2-thenoyltrifluoracetone (TTA) has been found useful for the extraction of a large number of metals. The review article by De and Khopkar[1] covers the literature up to 1961, since when about another 50 publications have appeared. TTA has now been applied to the extraction of rhenium(VII). With TTA, rhenium(VII) forms a colourless chelate which can be extracted with isoamyl alcohol-benzene from a sulphuric acid medium. For spectrophotometric evaluation of the rhenium(VII) the organic extract is treated with potassium thiocyanate and tin(II) chloride to give a yellow coloured product,[2] which can be measured at 430 mμ. This forms the basis of a new method for the extraction and spectrophotometric determination of rhenium(VII) at microgram level.

Earlier work on the ether extraction of rhenium thiocyanate complex has been described by Sandell.[2] 2,4-Diphenylthiosemicarbazide forms a red coloured product with rhenium and it is extractable into chloroform.[3] Rhenium, reduced with tin(II) chloride, can be extracted with benzildioxime-benzyl alcohol.[4] Tetraphenylarsonium chloride has been used to extract rhenium into chloroform.[5] In 4M sodium hydroxide solution rhenium has been extracted with pyridine.[6] Thio-oxine in chloroform can extract rhenium from a strong hydrochloric acid medium.[7] Methyl Violet in toluene[8] and diethylphosphorodithioic acid in benzene[9] have been reported to extract rhenium. Other extractants for this element include 4-methylcyclohexane-1,2-dione dioxime,[10] dimethylglyoxime,[11] α-furildioxime,[12] thiourea and diphenylthiourea[13] and toluene-3,4-dithiol.[14]

EXPERIMENTAL

Apparatus

A Unicam SP 600 spectrophotometer with 1-cm glass cells was used for the absorbance measurements.

Reagents

The reagents used were either chemically pure or reagent grade materials unless otherwise mentioned.

2-Thenoyltrifluoracetone (TTA). An approx. 0·15M solution of TTA (Columbia Organic Chemicals, Columbia, S. Carolina, U.S.A.) in isoamyl alcohol was used.

Stock solution of ammonium perrhenate. Prepared by dissolving ammonium perrhenate (Johnson, Matthey & Co. Ltd., London, England) in water containing 0·3*N* sulphuric acid. The solution, standardised by the nitron method,[15] contained 344 μg of rhenium/ml. Test solutions containing 34.4 μg of rhenium/ml were prepared by ten-fold dilution of the stock solution with 0·3*N* sulphuric acid.

20% *Potassium thiocyanate solution*

35% *Tin*(II) *chloride solution.* Prepared by dissolving 35 g of tin(II) chloride in 20 ml of 1:1 hydrochloric acid and diluting to 100 ml.

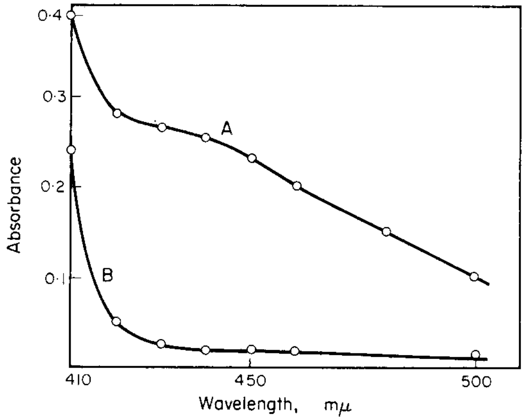


FIG. 1.—A. Absorption spectrum of rhenium thiocyanate [TTA chelate treated with tin(II) chloride-potassium thiocyanate] in isoamyl alcohol-benzene (Re = $1{\cdot}478 \times 10^{-5}M$; TTA = 0·15*M*; 7·6*N* sulphuric acid) *vs.* solvent mixture.
B. Reagent blank *vs.* solvent mixture.

General procedure

A suitable aliquot (0·5–4 ml) of ammonium perrhenate solution, containing 34·4 μg of rhenium/ml, was mixed with 10 ml of 7·6*N* sulphuric acid in a 250-ml separating funnel. For acidity studies, a suitable acid of desired strength was used. For the study of diverse ions, a solution containing the foreign ion was introduced before the addition of acid. Rhenium was extracted with 10 ml of 0·15*M* TTA in isoamyl alcohol plus 5 ml of benzene (pre-equilibrated with the acid) by shaking for 5 min, then the layers were allowed to settle and separate. The aqueous phase was titrated for the determination of acid when necessary and tested for the presence of rhenium (duplicate runs). To the separated organic phase 25 ml of 1:4 hydrochloric acid, 2 ml of 20% potassium thiocyanate and 1 ml of 35% tin(II) chloride were added and the mixture shaken for 5 min.[2] The resultant organic extract was filtered (to remove traces of water) into a 25-ml volumetric flask and diluted to 25 ml with isoamyl alcohol. The absorbance of this solution was then measured at 430 mμ against a reagent blank.

RESULTS AND DISCUSSION

Absorption curve

The absorption spectrum of a solution of the rhenium(VII)–TTA chelate extracted and processed as under *General procedure*, is shown in Fig. 1. All further measurements were carried out at 430 mμ where minimum reagent absorption occurs. The absorptivity at 430 mμ is 16240 ± 196.

Effect of acidity

The extraction of rhenium starts at an acidity of about 0·5*N* sulphuric acid, gradually increases and becomes 100% from 7·6*N* (equilibrium 7·12*N*) sulphuric acid onwards. This is shown in Fig. 2. The optimum acidity is 7·6–9·5*N* in sulphuric acid (equilibrium 7·12–9·04*N*). The distribution ratio in each case was calculated from the amount of rhenium in the organic phase and in the aqueous phase (the latter obtained by difference from the total amount taken), the values being recorded in Table I.

A hydrochloric acid medium is unsuitable because the extraction is incomplete.

The organic phase gave the test of rhenium(VII) only—with thiocyanate, colour was developed only after reduction with tin(II) chloride and furthermore, reaction with nitron gave a positive result. This ruled out the possibility of the existence of lower oxidation states of rhenium. The extracted species is presumably an ion-association compound having the structure:

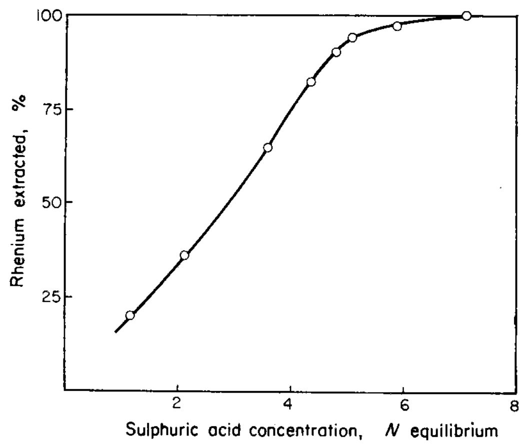
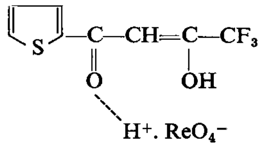


FIG. 2.—Extraction of rhenium-TTA chelate with isoamyl alcohol-benzene as a function of sulphuric acid concentration.



This is analogous to the cupferrate complex of pertechnetate, Cup^+. TcO_4^- reported by Elving *et al.*[16]

Calibration curve

The absorbances of different amounts of rhenium were measured at 410, 420, 430, 440 and 450 mμ against a reagent blank. The results prove that Beer's law is valid, as in the ether extraction method,[2] at 430 mμ over the concentration range of 0·5 to 6 μg of rhenium/ml.

The optimum TTA reagent concentration is 0·15M and the optimum period of extraction 5 min. The coloured system is stable for up to 2 hr, within which time measurements must be made.

Diverse ions

A number of binary mixtures of rhenium(VII) with other ions were prepared for the examination of interferences in the *General procedure* (7·6N sulphuric acid). The tolerance limit for each ion (Table II), represents that concentration of the foreign

TABLE I.—EXTRACTION OF RHENIUM (68·8 μg) AS A FUNCTION OF ACID CONCENTRATION

Sulphuric acid, *N* (equilibrium)	Distribution ratio,[a] *D*
1	0·17
1·17	0·20
2	0·41
2·09	0·45
3	0·86
3·58	1·48
4	2·4
4·34	3·66
4·8	7·28
5·09	13·4
5·88	28·83
6	39·2
6·5	79·2
7·12 to 9·04	100% extraction

[a] $$D = \frac{[\mathrm{Re}^{\mathrm{VII}}] \text{ per ml of organic phase}}{[\mathrm{Re}^{\mathrm{VII}}] \text{ per ml of aqueous phase}}.$$

TABLE II.—EFFECT OF DIVERSE IONS ON THE DETERMINATION OF RHENIUM (68·8 μg)

Diverse ion	Added as	Tolerance limit, μg
U^{6+}	$UO_2(NO_3)_2.6H_2O$	1000
Fe^{3+}	$FeCl_3.6H_2O$	1000
Cr^{3+}	$Cr_2(SO_4)_3.18H_2O$	5000
Mn^{2+}	$MnSO_4.5H_2O$	5000
Co^{2+}	$CoSO_4.7H_2O$	5000
Ni^{2+}	$NiSO_4.5H_2O$	5000
Cu^{2+}	$CuSO_4.5H_2O$	5000
Zr^{4+}	$ZrOCl_2$	5000
Th^{4+}	$Th(NO_3)_4.4H_2O$	5000
Ta^{5+}	Tantalum tartrate	1000
W^{6+}	Na_2WO_4	1000
PO_4^{3-}	$(NH_4)_2HPO_4$	10,000
F^-	NaF	10,000
Cl^-	NaCl	10,000
SCN^-	KSCN	10,000
EDTA	Disodium salt	10,000
Citrate	Citric acid	10,000
Tartrate	Tartaric acid	10,000
Oxalate	Sodium oxalate	10,000

ion in the presence of which the absorbance of rhenium is obtained within $\pm 2\%$. It should be noted that silver, zinc, bismuth, aluminium, mercury(II) and manganese(VII) do not show any interference even in large amounts. It is interesting that manganese(VII) is reduced by isoamyl alcohol in TTA solution and hence does not affect the extraction procedure. Thus, 68·8 μg of rhenium(VII) can be extracted in the presence of 100 times its amount of manganese(VII).

Palladium(II), molybdenum(VI), vanadium(V), titanium(IV), cerium(IV) and lead interfere, but moderate amounts of platinum(IV) and niobium(V) can be tolerated.

Molybdenum, if present, must be removed by a preliminary extraction. In the presence of mercury(I) nitrate and potassium thiocyanate,[17] molybdenum can be extracted with ether, then the rhenium can be extracted subsequently from the aqueous phase and measured as in the *General procedure*.

The interference from vanadium(V) and titanium(IV) can be removed by masking them with hydrogen peroxide in the acidic medium used. Cerium(IV) and palladium(II) can be eliminated by prior extraction at pH 6 with 0·5*M* TTA.

It should be possible to determine rhenium in fission residues by the proposed method. Thorium, zirconium, strontium, yttrium and caesium do not interfere. Uranium(VI) can be removed by preliminary extraction at pH 6 with TTA-benzene. Molybdenum and cerium (neodymium) can be removed as above.

With 68·8 μg of rhenium from ten runs, the absorbance measured was 0·24 ± 0·003. The sensitivity is 0·0112 μg/cm^2 (*cf.* 0·005 μg/cm^2 in the ether extraction method). The proposed method compares well with the standard ether extraction method as regards speed, accuracy and sensitivity.

It is superior to the standard ether method in that the solvent, *viz.* isoamyl alcohol-benzene, is much less volatile and more stable than ether; also in that the colour of the thiocyanate system is fairly stable and there is no deposition of solid on standing as in the ether method, leading to unsteady readings.

Analysis of an industrial material

Unfortunately, no rhenium-containing industrial material was available to the authors to test the proposed method for determination of rhenium. The method was, therefore, tested by introducing rhenium into a dissolved standard steel sample and ascertaining the recovery of rhenium.

A known weight (*ca.* 0·1 g) of alloy steel No. 64a (Bureau of Analysed Samples Ltd., Newham Hall, Yorks., U.K.; Fe 80%, Cr 4%, V 2%, Mo 4%, W 6%) was dissolved in sulphuric–nitric acids as described before,[18] 860 μg of rhenium (ammonium perrhenate) added and the solution made up to 100 ml. An aliquot of this solution (4 ml) was taken. Iron was first removed by adjusting the pH to 1 and extracting with two 50-ml portions of acetylacetone-chloroform (50%). To the aqueous phase was added concentrated sulphuric acid to make the solution 2*N* in this acid, molybdenum reduced with mercury(I) nitrate and the solution treated with thiocyanate and extracted with ether as described before. The residual aqueous phase was evaporated to about 2 ml, and 20 ml of 12*N* sulphuric acid and 5 ml of 20 vol. hydrogen peroxide added. Vanadium was masked and rhenium extracted with TTA and determined as under *General procedure*. Chromium(III) and tungsten(VI) did not interfere in the analytical range used.

The results from triplicate analysis as above were: 838, 848 and 840 μg of rhenium (rhenium taken: 860 μg).

Zusammenfassung—Eine neue Methode zur Bestimmung von Rhenium(VII) im Mikrogrammbereich wird vorgeschlagen. 2-Thenoyltrifluoraceton in Isoamylalkohol-Benzol extrahiert Rhenium(VII) quantitativ aus 7–9 n Schwefelsäure. Behandlung des organischen Extrakts mit Zinn(II)-chlorid und Kaliumrhodanid gibt ein gelbes Produkt, das bei 430 mμ photometriert werden kann. Das Beersche Gesetz gilt von 0,5 bis 5 μg Rhenium im ml. Der Einfluß verschiedener Ionen wurde untersucht.

Résumé—On propose une nouvelle méthode de dosage du rhénium(VII) à l'échelle du microgramme. La 2-thénoyltrifluoracétone en alcool isoamylique-benzène extrait quantitativement le rhénium(VII) à partir de ses solutions dans l'acide sulfurique 7–9 N. Le traitement de cet extrait organique par le chlorure stanneux et le sulfocyanure de potassium donne un produit coloré en jaune que l'on peut mesurer à 430 mμ. La loi de Beer est respectée pour des concentrations en rhénium comprises entre 0,5 et 5 μg/ml. On a étudié l'influence de divers ions.

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PRECIPITATION OF ZINC SULPHIDE FROM AMMONIACAL SOLUTIONS BY THIOACETAMIDE*

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Summary—The rate at which thioacetamide precipitates zinc sulphide from ammoniacal zinc solutions is controlled mainly by two types of reaction: reactions between the various zinc species and thioacetamide, and reactions between the zinc and the sulphide produced by an ammonia-thioacetamide reaction; the sulphide from the hydroxide catalysed hydrolysis of thioacetamide is relatively small. The rate expression for reactions of the first type is

$$-\frac{d[Zn(II)]}{dt} = \sum_{n=0}^{4} k_n[CH_3CSNH_2][Zn(NH_3)_n{}^{2+}][H^+]^{-2/3}.$$

The rate of precipitation by the second process is controlled by the rate at which sulphide is formed by the ammonia-thioacetamide reaction; this rate expression is

$$-\frac{d[CH_3CSNH_2]}{dt} = -\frac{d[Zn(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2.$$

INTRODUCTION

STUDIES carried out in these laboratories of the rates of precipitation of various metal sulphides by thioacetamide [TAA] have shown that these precipitation rates are controlled by either or both of two types of reaction process. These studies indicate that one of these processes involves a reaction between the metal and TAA; the second process involves a reaction between the metal and the sulphide produced by reaction of TAA with one or more constituents in the solution. In the cases studied the rate of precipitation by this latter process is the same as the rate of production of sulphide; therefore, the rate expression for the precipitation is identical with that for the production of sulphide. Rate studies have been made of the production of sulphide from TAA by hydrolysis catalysed by acid[1] and by base,[2] by reactions in ammonia-ammonium chloride and in carbonate-hydrogen carbonate buffers[3] and by reaction with hydrazine.[4]

The precipitation of zinc sulphide from acid solutions has been found[5] to proceed by both the direct reaction and the acid catalysed hydrolysis reaction. The rate equation for this precipitation at 90°, in units of moles, litres and minutes, is

$$-\frac{d[Zn^{2+}]}{dt} = 4{\cdot}2 \times 10^{-4}\,\frac{[Zn^{2+}][CH_3CSNH_2]}{[H^+]^{1/2}} + 0{\cdot}23\,[H^+][CH_3CSNH_2].$$

The present paper extends the study of the precipitation of zinc sulphide by TAA to ammoniacal solutions. Precipitation of metals from ammonia buffer systems is of

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* Contribution No. 3144.

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interest because of the high stability of many metal-ammonia complexes, and because by control of the ammonia-TAA reaction one can vary the rate of sulphide formation at constant pH.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used throughout. The TAA was Arapahoe Chemical Co. material. Stock solutions were prepared and, when necessary, were standardised by conventional methods. Disodium ethylenediaminetetra-acetate (EDTA) solution, 0·01 *VF* (volume formal), was standardised against metallic zinc.

Procedure

A reaction solution was prepared from distilled water and stock solutions of ammonia, ammonium nitrate and zinc nitrate, and the ionic strength was adjusted to 0·65 with sodium nitrate when necessary. The solution, contained in a 38 × 200 mm-stoppered test tube, was preheated to slightly above 40°, the desired volume of TAA solution at room temperature added and the tube immersed in a water bath at 40 ± 0·5°. At timed intervals a sample of the suspension was removed and rapidly filtered through a fritted glass filter. Duplicate 5.00-ml aliquots of this filtrate were then acidified and boiled to destroy the excess thioacetamide and volatilise the hydrogen sulphide formed. These solutions were adjusted to a pH of about 10 with an ammonia-ammonium chloride buffer, and the zinc was titrated with the EDTA solution; Eriochrome Black T was used as indicator.

The initial over-all rate of precipitation was obtained from the experimental points by graphical methods. The reactions were followed until about 20–30% of the zinc had precipitated.

RESULTS AND DISCUSSION

The symbol [Zn(II)] represents the total (volume formal) concentration of zinc in the solution; therefore, $[\mathrm{Zn(II)}] = \sum_{n=0}^{4} [\mathrm{Zn(NH_3)_n}^{2+}]$. The ammonia concentrations given in the rate expressions are the free ammonia concentrations, *i.e.*, the total concentration of ammonia added less the amount present in zinc ammines.

Ammonia-thioacetamide reaction

Peters and Swift[3] have studied the reactions of thioacetamide in ammonia buffers over the temperature range of 60° to 90°. The rate of production of sulphide is described by the following equation:

$$-\frac{d[\mathrm{CH_3CSNH_2}]}{dt} = k[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2$$

where $k = 0{\cdot}055 \pm 0{\cdot}001$ litre^2.mole^{-2}.min^{-1} at 90°, and 0·012 at 60°.

The present work was carried out at 40°, and the corresponding value of k was determined, using a method similar to that of Peters and Swift. Seven experiments gave a mean value of k at 40° of $(5{\cdot}0 \pm 0{\cdot}2) \times 10^{-3}$ litre^2.mole^{-2}.min^{-1}.

The sulphide produced by the ammonia-thioacetamide reaction was assumed to react rapidly and quantitatively to form zinc sulphide. Therefore, the rate of precipitation of zinc sulphide by the ammonia-thioacetamide reaction could be calculated from the expression

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = 5{\cdot}0 \times 10^{-3}[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2.$$

Direct reaction

Under the conditions of this study, both the ammonia-thioacetamide reaction and the direct reaction took place to a significant extent. The reaction rate observed was the sum of the two reaction rates, from which the rate of the direct reaction was obtained by difference.

Effect of zinc and thioacetamide concentrations

Table I shows the results of experiments in which the initial thioacetamide concentration was varied from 0·0100*VF* to 0·0500*VF* at initial zinc concentrations of 0·0100 and 0·00250*VF*. When necessary, the total ammonia concentration was so varied as to keep the concentration of uncomplexed ammonia constant. The values in Table I indicate that the rate of the direct reaction is first order with respect to both zinc and thioacetamide.

TABLE I.—EFFECT OF ZINC AND THIOACETAMIDE CONCENTRATIONS ON THE INITIAL RATE OF PRECIPITATION OF ZINC SULPHIDE

TAA, *VF*	Zn(II), *VF*	Observed rate of precipitation, *mole.litre*$^{-1}$*.min*$^{-1}$	Calculated rate of NH_3—CH_3CSNH_2 reaction,[a] *mole.litre*$^{-1}$*.min*$^{-1}$	Calculated rate of direct reaction, *mole.litre*$^{-1}$*.min*$^{-1}$	K'_{direct},[b] *litre.mole*$^{-1}$*.min*$^{-1}$
0·0100	0·0100	1·65 × 10^{-5}	0·07 × 10^{-5}	1·58 × 10^{-5}	0·158
0·0150	0·0100	2·58	0·10	2·48	0·165
0·0200	0·0100	3·44	0·13	3·31	0·165
0·0500	0·0100	8·39	0·32	8·07	0·161
0·0100	0·00250[c]	0·418	0·066	0·352	0·160

(Initial conditions: total NH_3 = 0·154*VF*; calculated free $[NH_3]$ = 0·115*VM*; $[NH_4^+]$ = 0·265*VM*; pH = 8·41, temperature = 40°.)

[a] Calculated from expression $\frac{-d[Zn(II)]}{dt} = 5{\cdot}0 \times 10^{-3}[CH_3CSNH_2][NH_3]^2$.

[b] Calculated from expression $\frac{-d[Zn(II)]}{dt} = K'[CH^3CSNH_2][Zn(II)]$.

[c] Initial total NH_3 = 0·125*VF*; initial free $[NH_3]$ = 0·115*VM*.

Effect of ammonia concentration

Bjerrum[6] has found that zinc forms four ammine complexes in aqueous solutions, and has determined the formation constants. The general equilibrium expression for their formation is

$$\frac{[Zn(NH_3)_n{}^{2+}]}{[Zn(NH_3)_{n-1}^{2+}][NH_3]} = K_n.$$

For each concentration of free ammonia the relative concentration of each zinc-ammine and n̄, the average coordination number of zinc, were calculated. This information is presented in Table II. The concentration of the aquated zinc ion is negligible and not included in the calculations below.

TABLE II.—EFFECT OF FREE AMMONIA CONCENTRATION ON THE CONCENTRATION OF ZINC AMMINES

Free $[NH_3]$, *VM*	Average co-ordination number, n̄	Percentage of total zinc present as			
		$Zn(NH_3)_4{}^{2+}$	$Zn(NH_3)_3{}^{2+}$	$Zn(NH_3)_2{}^{2+}$	$Zn(NH_3)^{2+}$
0·280	3·97	96·0	3·93	0·07	—
0·115	3·89	89·8	9·79	0·47	—
0·0800	3·84	85·5	13·4	0·94	0·08
0·0600	3·79	81·0	17·3	1·66	0·18
0·0400	3·69	73·0	23·1	3·34	0·53

Fig. 1 shows the dependence of the initial precipitation rates, both of the total reaction and of the direct reaction, upon the ammonia concentration. The observed relationship between the ammonia concentration and the rate of the direct reaction may be attributed to different rates of reaction of the various zinc-ammine species with thioacetamide. Individual second-order rate constants, k_n', for each zinc-ammine species were computed from a system of simultaneous equations based on the values in Fig. 1 and Table II. These equations were of the following form:

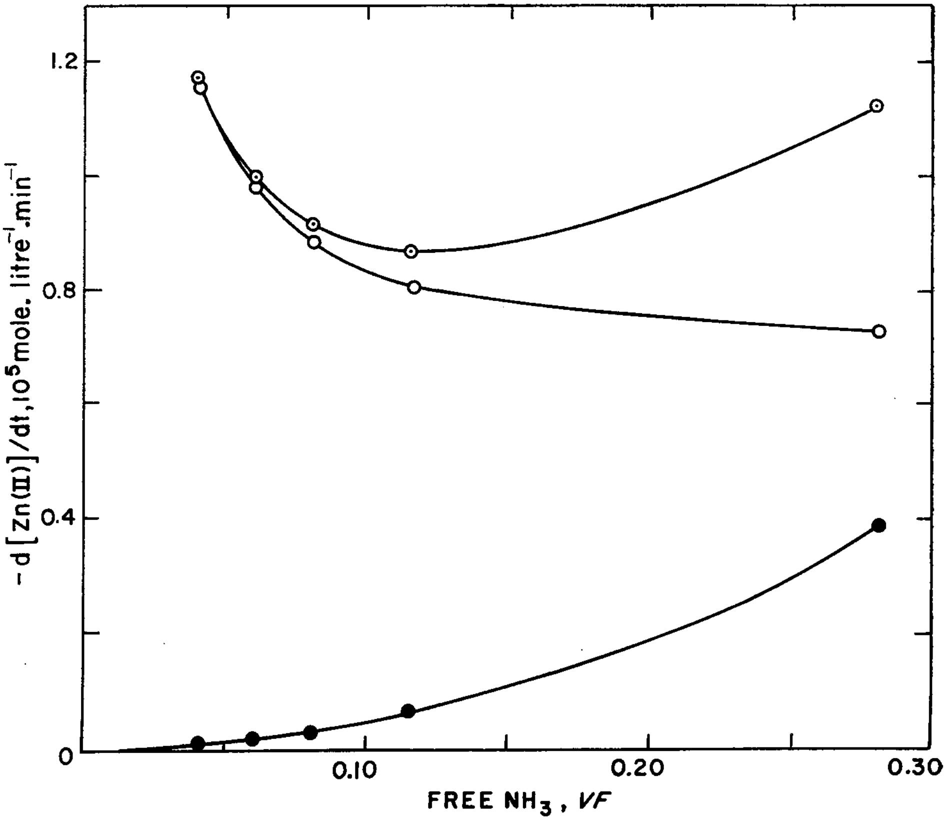

FIG. 1.—Effect of ammonia concentration on rate of precipitation of zinc sulphide (initial conditions: [Zn(II)] = 0·01 *VF*; CH_3CSNH_2 = 0·005 *VF*; pH = 8·41; temperature = 40°):—

⊙—over-all reaction,
○—direct reaction,
●—NH_3–TAA reaction.

$$-\frac{d[Zn(II)]}{dt} = [Zn(II)][CH_3CSNH_2]\left(k_4' \frac{[Zn(NH_3)_4^{2+}]}{[Zn(II)]} + k_3' \frac{[Zn(NH_3)_3^{2+}]}{[Zn(II)]} + k_2' \frac{[Zn(NH_3)_2^{2+}]}{[Zn(II)]} + k_1' \frac{[Zn(NH_3)^{2+}]}{[Zn(II)]}\right).$$

It can be seen that K′, as given in Table I, corresponds to the term in parentheses in the above equation.

The best values of the individual second-order rate constants are:

$$k_4' = 0{\cdot}136, \quad k_3' = 0{\cdot}39, \quad k_2' = 0{\cdot}93, \quad k_1' = 2{\cdot}3 \text{ litre.mole}^{-1}\text{.min}^{-1}.$$

Effect of pH

The effect of pH on the direct reaction was studied over a pH range of 8·12 to 9·13. The results presented in Table III indicate that the rate of the direct reaction is inversely proportional to the two-thirds power of the hydrogen ion concentration.

TABLE III.—EFFECT OF pH ON THE INITIAL RATE OF PRECIPITATION OF ZINC SULPHIDE

pH	Observed rate of precipitation, *mole.litre⁻¹.min⁻¹*	Calculated rate of direct reaction,[a] *mole.litre⁻¹.min⁻¹*	K'_{direct},[b] *litre.min⁻¹.mole⁻¹*	K'',[c] *litre^1/3.mole^−1/3.min⁻¹*
9·13	$4{\cdot}75 \times 10^{-5}$	$4{\cdot}62 \times 10^{-5}$	0·462	$3{\cdot}84 \times 10^{-7}$
8·84	3·06	2·93	0·293	3·80
8·41	1·74	1·61	0·161	3·90
8·12	1·12	0·99	0·099	3·85

(Initial conditions: [Zn(II)] = 0·005*VF*; $[CH_3CSNH_2]$ = 0·0200*VM*; total NH_3 = 0·134*VF*; free $[NH_3]$ = 0·115*VM*; temperature = 40°.)

[a] Obtained from observed over-all rate by subtracting the rate of the ammonia-thioacetamide reaction, $0{\cdot}13 \times 10^{-5}$ mole.litre⁻¹.min⁻¹.

[b] Calculated from the expression $-d[Zn(II)]/dt = K'[CH_3CSNH_2][Zn(II)]$.

[c] Calculated from the expression $-d[Zn(II)]/dt = K''[CH_3CSNH_2][Zn(II)]/[H^+]^{2/3}$.

According to Bjerrum[6] the formation constants of the various metal ammines depend on the ammonium nitrate concentration; however, the variation in the ammonium ion concentrations was not large enough to affect significantly the relative concentrations of the various ammines.

Rate expression

The true rate constants, k_n, may be obtained from the second-order constants, k_n', measured at pH 8·41. The values of the true rate constants at 40°, expressed in $\text{litre}^{1/3}\text{.mole}^{-1/3}\text{.min}^{-1}$, are:

$$k_4 = 3{\cdot}1 \times 10^{-7}, \quad k_3 = 8{\cdot}9 \times 10^{-7}, \quad k_2 = 21 \times 10^{-7}, \quad k_1 = 53 \times 10^{-7}.$$

It can be seen that as n decreases by 1, the rate constant increases by a factor of about 2·5. Therefore, k_0, the rate constant for the completely aquated zinc ion, may be estimated as $1{\cdot}3 \times 10^{-5}$. Bowersox, Smith and Swift[5] have studied the thioacetamide precipitation of zinc sulphide from non-complexing acidic media at 90°. Extrapolation of their data to 40° yields a value of the direct reaction rate constant of 1×10^{-5}. The agreement between this value and the estimated value of k_0 is surprising in view of the fact that in acidic media the rate varies inversely with the square root of the hydrogen ion concentration, while in the present work the rate varies inversely with the two-thirds root.

The kinetic expression for the over-all rate of precipitation of zinc sulphide from an ammoniacal solution by thioacetamide at 40° is as follows, in units of moles, litres and minutes:

$$-\frac{d[Zn(II)]}{dt} = \frac{10^{-7}[CH_3CSNH_2]}{[H^+]^{2/3}}(3{\cdot}1[Zn(NH_3)_4{}^{2+}] + 8{\cdot}9[Zn(NH_3)_3{}^{2+}] + 21[Zn(NH_3)_2{}^{2+}] + 53[Zn(NH_3)^{2+}] + 130[Zn^{2+}]) + 5{\cdot}0 \times 10^{-3}[CH_3CSNH_2][NH_3]^2.$$

Precipitation at high concentrations of zinc and thioacetamide

At concentrations of zinc and thioacetamide somewhat higher than those in the above experiments, and particularly at the lower ammonia concentrations, the behaviour of the system differed from that previously observed, the most apparent change being the precipitation of as much as four-fifths of the zinc during the mixing process. When this initial rapid precipitation was not observed, the course of the reaction was adequately described by the above rate expression and rate constants. Although the rate data from each experiment with concentrated solutions fit the expression

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = K'_{\mathrm{direct}}[\mathrm{Zn(II)}]$$

the value found for K'_{direct} depended strongly upon the method of addition of thioacetamide to the reaction mixture, the age of the thioacetamide solution and the presence of added seed crystals of zinc sulphide in the reaction mixture. This variation in rate, caused by nucleation effects, has been investigated and will be reported separately.[7]

ANALYTICAL CONSIDERATIONS

The zinc-sulphide precipitate obtained with thioacetamide was relatively dense and granular and, therefore, could be readily separated from the supernatant by filtration or centrifugation.

The results presented here suggest that with suitable modification of procedure thioacetamide may be substituted for hydrogen sulphide as a sulphide precipitant in ammoniacal systems. The dependence of the rates of both the direct reaction and the ammonia-thioacetamide reaction on the ammonia concentration permit the over-all precipitation rate to be varied over rather wide limits, even at constant temperature and pH. This increased control over the precipitation rate would seem to be advantageous in carrying out effective separations in ammoniacal media; however, no definite conclusions concerning separations can be drawn until the behaviour of each combination of elements involved has been studied.

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Zusammenfassung—Die Geschwindigkeit der Fällung von Zinksulfid aus ammoniakalischen Lösungen mit Thioacetamid wird hauptsächlich durch zwei Reaktionstypen kontrolliert: Reaktionen zwischen den verschiedenen Zinkspezies und Thioacetamid und Reaktionen zwischen Zink und dem aus der Reaktion zwischen Ammoniak und Thioacetamid stammenden Sulfid; die aus der durch Hydroxylionen katalysierten Hydrolyse von Thioacetamid stammende Sulfidmenge ist relativ klein. Die Geschwindigkeitsgleichung für Reaktionen des ersten Typs ist

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = \sum_{n=0}^{4} k_n[\mathrm{CH_3CSNH_2}][\mathrm{Zn(NH_3)_n}^{2+}][\mathrm{H^+}]^{-2/3}.$$

Die Fällungsgeschwindigkeit nach dem zweiten Prozeß wird durch Geschwindigkeit der Sulfidbildung aus Ammoniak und Thioacetamid bestimmt; dieser Geschwindigkeitsausdruck lautet

$$-\frac{d[\mathrm{CH_3CSNH_2}]}{dt} = -\frac{d[\mathrm{Zn(II)}]}{dt} = k[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2.$$

Résumé—On contrôle la vitesse à laquelle le thioacétamide précipite le sulfure de zinc à partir de solutions ammoniacales de zinc essentiellement par deux types de réactions: réactions entre les différentes espèces du zinc et la thioacétamide, et réactions entre le zinc et le sulfure produit par une réaction ammoniaque-thioacétamide; le sulfure produit par l'hydrolyse du thioacétamide catalysée par l'hydroxyde est relativement faible. L'équation de vitesse pour les réactions du premier type est:

$$-\frac{d[Zn(II)]}{dt} = \sum_{n=0}^{4} k_n[CH_3CSNH_2][Zn(NH_3)_n{}^{2+}][H^+]^{-2/3}.$$

La vitesse de précipitation selon le second processus est contrôlée par la vitesse à laquelle se forme le sulfure dans la réaction ammoniaque-thioacétamide; cette équation de vitesse est:

$$-\frac{d[CH_3CSNH_2]}{dt} = -\frac{d[Zn(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2.$$

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PRECIPITATION OF NICKEL SULPHIDE FROM AMMONIACAL SOLUTIONS BY THIOACETAMIDE[†]

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Summary—The rate of precipitation of nickel sulphide from ammoniacal solutions by thioacetamide is controlled mainly by two types of reaction: reactions between the various nickel species and thioacetamide, and reactions between the nickel species and the sulphide produced by a thioacetamide-ammonia reaction. The sulphide produced by the hydroxide-catalysed hydrolysis of thioacetamide is relatively small. The rate expressions for these two predominant processes are, respectively,

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = \sum_{n=0}^{6} k_n[\mathrm{Ni(NH_3)_n}^{2+}][\mathrm{CH_3CSNH_2}][\mathrm{H^+}]^{-2/3}$$

and

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = k[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2.$$

INTRODUCTION

PREVIOUS studies of the rates of precipitation of metal sulphides by thioacetamide (TAA) have indicated that two processes are involved in these precipitations. In one of these the TAA reacts with some constituent of the solution to liberate sulphide, which then forms the precipitate; in such cases the rate of sulphide formation limits the rate of the precipitation. Precipitation by the other process occurs without the intermediate formation of sulphide from TAA. In the latter case the reaction appears to take place directly between the metal ion and TAA; this process is called the *direct reaction.*

Within the accuracy of the measurements, the rate of precipitation of nickel sulphide from acidic solutions has been found to be controlled by the direct reaction only.[2] The rate equation for this precipitation at 90°, in units of moles, litres and minutes, is

$$-\frac{d[\mathrm{Ni^{2+}}]}{dt} = 2{\cdot}2 \times 10^{-4}\,[\mathrm{Ni^{2+}}][\mathrm{CH_3CSNH_2}][\mathrm{H^+}]^{-1/2}.$$

An experimental study[3] of the precipitation of zinc sulphide by TAA from solutions buffered by ammonia and ammonium ion has indicated that the hydrated zinc ion and the zinc ammines are precipitated *via* both routes. The direct reaction with each zinc species is characterised by a different value of the direct-reaction rate constant.

A study of the precipitation of nickel sulphide by TAA from ammoniacal solutions is presented here. In such solutions, sulphide is produced predominantly by a TAA-ammonia reaction, the rate of which depends upon the square of the ammonia

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concentration. Washizuke[4] has reported that precipitation occurs by a different mechanism in more concentrated ammonia solutions (0·4–1·2*M*); in these solutions the rate of precipitation of nickel sulphide appears to be dependent on the rate of a base-catalysed reaction between TAA, NH_3 and OH. In the present systems, and in those studied by Washizuke, the rate of precipitation by processes other than the direct reaction can be controlled by varying the ammonia concentration.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used throughout. The TAA was Arapahoe Chemical Company material. Stock solutions were prepared and, when necessary, were standardised by conventional methods. The reaction solutions were prepared from distilled water and stock solutions of ammonia, ammonium nitrate and nickel(II) nitrate. The ionic strength of the reaction solutions was adjusted to 0·30 with sodium nitrate.

Procedure

The solution, contained in a 38 × 200-mm stoppered test tube, was preheated to slightly above 40°, the appropriate volume of TAA solution at room temperature added and the tube immersed in a water bath at 40° ± 0·5°. At timed intervals a sample of the suspension was removed and filtered through a fritted glass filter into a tube containing solid disodium ethylenediaminetetra-acetate (EDTA). The excess solid EDTA was removed by filtration, and the concentration of nickel in the solution determined colorimetrically. Confirmatory analyses showed that this procedure gave results reproducible to within 3%.

The initial rates of precipitation reported below were obtained graphically from the experimental points. The reactions were followed only until approximately 20% of the nickel was precipitated; this reduced the effect of the increase in ammonia concentration caused by release of ammonia from the nickel ammines.

RESULTS AND DISCUSSION

In the subsequent discussion, the symbol [Ni(II)] represents the total (volume formal) concentration of nickel in solution; therefore

$$[\mathrm{Ni(II)}] = \sum_{n=0}^{6} [\mathrm{Ni(NH_3)_n{}^{2+}}].$$

The ammonia concentrations shown in the rate expressions are for free ammonia.

Ammonia-thioacetamide reaction

The rate of precipitation of nickel sulphide as a result of this reaction was assumed to be equal to the calculated rate of formation of sulphide. The rate expression is therefore

$$-\frac{d[\mathrm{CH_3CSNH_2}]}{dt} = -\frac{d[\mathrm{Ni(II)}]}{dt} = k\,[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2.$$

The value of the rate constant k at 40° has been found[2] to be $5{\cdot}0 \times 10^{-3}$ $\mathrm{litre^2.\ mole^{-2}.\ min^{-1}}$.

Effect of nickel and thioacetamide concentrations

Table I presents the results of experiments in which the initial nickel and TAA concentrations were varied at constant pH and free ammonia concentration. The results indicate that the direct reaction rate is dependent on the first order of both Ni(II) and TAA concentration.

Effect of pH

The rate of the direct reaction was studied over the pH range of 8·67 to 9·49. As shown in Table I, at these hydrogen-ion concentrations, the rate appears to be inversely proportional to the two-thirds power of the hydrogen-ion concentration.

TABLE I.—EFFECT OF NICKEL, THIOACETAMIDE AND HYDROGEN-ION CONCENTRATIONS ON THE INITIAL RATE OF PRECIPITATION OF NICKEL SULPHIDE

TAA, *VF*	Ni(II), *VF*	pH	$[H^+]^{2/3}$, *VM*	Observed rate, *mole. litre⁻¹. min⁻¹*	Rate of direct reaction,[a] *mole. litre⁻¹. min⁻¹*	K,[b] *mole. litre⁻¹. min⁻¹*
0·100	0·0100	9·22	$7·1 \times 10^{-7}$	$3·0 \times 10^{-5}$	$2·7 \times 10^{-5}$	$1·9 \times 10^{-8}$
0·200	0·0100	9·22	$7·1 \times 10^{-7}$	$6·3 \times 10^{-5}$	$5·7 \times 10^{-5}$	$2·0 \times 10^{-8}$
0·100	0·0200	9·22	$7·1 \times 10^{-7}$	$6·0 \times 10^{-5}$	$5·7 \times 10^{-5}$	$2·0 \times 10^{-8}$
0·150	0·0100	8·67	$1·7 \times 10^{-6}$	$3·2 \times 10^{-5}$	$2·7 \times 10^{-5}$	$2·0 \times 10^{-8}$
0·100	0·0100	8·94	$1·1 \times 10^{-6}$	$2·1 \times 10^{-5}$	$1·8 \times 10^{-5}$	$2·0 \times 10^{-8}$
0·100	0·0100	9·49	$4·7 \times 10^{-7}$	$4·7 \times 10^{-5}$	$4·4 \times 10^{-5}$	$2·1 \times 10^{-8}$

(Free NH_3 = 0 080 *VM*; temperature = 40°.)

[a] Calculated from observed rate by subtracting the rate of the NH_3–TAA reaction, $5·0 \times 10^{-3}$ $[CH_3CSNH_2]\,[NH_3]^2$.

[b] Calculated from the expression K = rate of direct reaction multiplied by

$$\frac{[H^+]^{2/3}}{[CH_3CSNH_2][Ni(II)]} \cdot$$

Effect of ammonia concentration

Nickel in aqueous solution forms six ammine complexes, the general equilibrium expression for their formation being

$$\frac{[Ni(NH_3)_n{}^{2+}]}{[Ni(NH_3)_{n-1}][NH_3]} = K_n \, .$$

Bjerrum[1] has determined the values of K_n. Therefore, for each concentration of free ammonia, the relative concentration of each nickel ammine and the average number of ammonia molecules co-ordinated to each nickel ion, ñ, could be computed. This information is presented in Table II.

Table III shows the dependence of the initial rates of the over-all precipitation and the direct reaction on the free ammonia concentration. At free ammonia concentrations greater than approximately 0·3 molal, the rate of the ammonia–TAA reaction becomes so fast that the direct reaction process makes a relatively small contribution to the over-all precipitation rate. The observed relationship between rate and ammonia concentration for the direct reaction may be explained by assuming that each nickel species reacts at a different rate. In principle, therefore, a series of simultaneous equations of the form

$$-\frac{d[Ni(II)]}{dt} = [CH_3CSNH_2](k_0'[Ni^{2+}] + k_1'[Ni(NH_3)^{2+}] \\ + k_2'[Ni(NH_3)_2{}^{2+}] + \ldots + k_6'[Ni(NH_3)_6{}^{2+}])$$

could be set up and solved for the value of k_n'. It was observed in the analogous case of zinc,[3] however, that the ratios of successive rate constants were approximately constant, *i.e.*, that $k_0'/k_1' = k_1'/k_2' = k_2'/k_3'$, *etc.* In order to simplify the computations, the assumption was made that the ratios of successive rate constants are also

TABLE II.—EFFECT OF FREE AMMONIA CONCENTRATION ON THE RELATIVE CONCENTRATIONS OF NICKEL AMMINES

Free $[NH_3]$, *VM*	Average ammonias per nickel, $\bar{n}$	$[Ni^{2+}]$	$[Ni(NH_3)^{2+}]$	$[Ni(NH_3)_2{}^{2+}]$	$[Ni(NH_3)_3{}^{2+}]$	$[Ni(NH_3)_4{}^{2+}]$	$[Ni(NH_3)_5{}^{2+}]$	$[Ni(NH_3)_6{}^{2+}$
0·060	3·13	0·00121	0·0286	0·204	0·436	0·268	0·0596	0·00254
0·080	3·38	0·00048	0·0155	0·143	0·405	0·332	0·0986	0·00558
0·110	3·64	0·00016	0·00702	0·0884	0·345	0·389	0·158	0·0125
0·150	3·90	0·00005	0·00296	0·0509	0·272	0·418	0·232	0·0247
0·200	4·14	—	0·00124	0·0286	0·203	0·416	0·309	0·0436
0·250	4·32	—	0·00061	0·0174	0·154	0·396	0·367	0·0650

TABLE III.—EFFECT OF FREE AMMONIA CONCENTRATION ON THE INITIAL RATE OF PRECIPITATION OF NICKEL SULPHIDE

Free $[NH_3]$, *VM*	Ni(II), *VF*	TAA, *VF*	Observed rate, *mole. litre*$^{-1}$*. min*$^{-1}$	Rate of direct reaction,[a] *mole. litre*$^{-1}$*. min*$^{-1}$	K',[b]	Computed rate,[c]
0·050	0·0100	0·0500	$2\cdot9 \times 10^{-5}$	$2\cdot8 \times 10^{-5}$	$5\cdot6 \times 10^{-2}$	$2\cdot8 \times 10^{-5}$
0·060	0·0100	0·100	$4\cdot5 \times 10^{-5}$	$4\cdot3 \times 10^{-5}$	$4\cdot3 \times 10^{-2}$	$4\cdot3 \times 10^{-5}$
0·080	0·0100	0·100	$3\cdot1 \times 10^{-5}$	$2\cdot8 \times 10^{-5}$	$2\cdot8 \times 10^{-2}$	$2\cdot8 \times 10^{-5}$
0·110	0·0100	0·150	$3\cdot6 \times 10^{-5}$	$2\cdot7 \times 10^{-5}$	$1\cdot8 \times 10^{-2}$	$2\cdot5 \times 10^{-5}$
0·150	0·0300	0·100	$4\cdot4 \times 10^{-5}$	$3\cdot3 \times 10^{-5}$	$1\cdot1 \times 10^{-2}$	$3\cdot3 \times 10^{-5}$
0·200	0·0200	0·200	$6\cdot9 \times 10^{-5}$	$2\cdot9 \times 10^{-5}$	$0\cdot72 \times 10^{-2}$	$2\cdot9 \times 10^{-5}$
0·250	0·0300	0·200	$7\cdot4 \times 10^{-5}$	1×10^{-5}	$0\cdot18 \times 10^{-2}$	3×10^{-5}
0·200[d]	0·0200	0·100	5×10^{-5}	3×10^{-5}	—	2×10^{-5}
0·293[d]	0·0200	0·200	13×10^{-5}	4×10^{-5}	—	4×10^{-5}

(pH = 9·22; temperature = 40°)

[a] Computed from observed rate by subtracting the rate of the NH_3–TAA reaction; $5\cdot0 \times 10^{-3}$ $[CH_3CSNH_2]\,[NH_3]^2$.

[b] Computed from the expression $K' = \dfrac{\text{Rate of direct reaction}}{[CH_3CSNH_2]\,[Ni(II)]}$.

[c] Computed from the second-order rate constants for each nickel ammine species.

[d] pH = 10·04.

constant for the nickel ammines. Based on this assumption the best values of the individual second order rate constants, k_n', expressed in litre. mole^{-1}. min^{-1}, are

$$\begin{aligned} k_0' &= 2\cdot9 \\ k_1' &= 5\cdot0 \times 10^{-1} \\ k_2' &= 8\cdot6 \times 10^{-2} \\ k_3' &= 1\cdot5 \times 10^{-2} \\ k_4' &= 2\cdot5 \times 10^{-3} \\ k_5' &= 4\cdot4 \times 10^{-4} \\ k_6' &= 7\cdot5 \times 10^{-5}. \end{aligned}$$

The rates of the direct reaction calculated on the basis of these rate constants are also presented in Table III.

Rate expression

The true rate constants, k_n, were obtained from the second order constants, k_n', measured at pH 9·22 and 40°. The best values for these constants, in units of moles, litres and minutes, are incorporated into the following equation, which describes the over-all rate of precipitation of nickel sulphide from ammoniacal solution by thioacetamide at 40°.

$$
\begin{aligned}
-\frac{d[Ni(II)]}{dt} = {} & 5{\cdot}0 \times 10^{-3}[CH_3CSNH_2][NH_3]^2 + \frac{[CH_3CSNH_2]}{[H^+]^{2/3}}(2{\cdot}1 \times 10^{-6}[Ni^{2+}] \\
& + 3{\cdot}5 \times 10^{-7}[Ni(NH_3)^{2+}] + 6{\cdot}0 \times 10^{-8}[Ni(NH_3)_2{}^{2+}] + 1{\cdot}0 \\
& \times 10^{-8}[Ni(NH_3)_3{}^{2+}] + 1{\cdot}8 \times 10^{-9}[Ni(NH_3)_4{}^{2+}] + 3{\cdot}0 \\
& \times 10^{-10}[Ni(NH_3)_5{}^{2+}] + 5{\cdot}3 \times 10^{-11}[Ni(NH_3)_6{}^{2+}]).
\end{aligned}
$$

Effect of temperature

To determine the dependence of the precipitation on temperature, experiments were performed at 25°, 40°, 50°, 60° and 70° with solutions in which the initial concentrations of the reagents were as follows: [Ni(II)] = 0·0200*VF*; CH_3CSNH_2 = 0·0500*VF*; NH_4Cl = 0·060*VF*; total initial NH_3 = 0·38*VF*; and calculated free ligand NH_3 = 0·29*VM*. The initial rates for each temperature are given in Table IV. Because of uncertainties concerning the values of the formation constants of the nickel ammines at the higher temperatures, and because of the likelihood of volatilisation of some of the ammonia, no attempts were made to calculate the temperature dependence of the ammonia-TAA or the direct-reaction processes.

TABLE IV.—EFFECT OF TEMPERATURE ON RATE OF PRECIPITATION

Temperature, °*C*	Initial over-all rate of precipitation, × 10^5
25	0·9
40	4·5
50	8
60	18
70	50

Initial Conditions: Ni(II) = 0·020*VF*; CH_3CSNH_2 = 0·050*VF*; NH_4Cl = 0·060*VF*; free ligand NH_3 = 0·29*VM*; total initial NH_3 = 0·38*VF*.

ANALYTICAL CONSIDERATIONS

These studies have shown that the rate of precipitation of nickel sulphide by thioacetamide can be varied over a wide range by the proper selection of the reaction temperature and the concentrations of the reagents. For example, calculations indicate that in a solution initially 0·01*VF* in nickel(II), 0·10*VF* in thioacetamide, 0·30*VF* in free ammonia and having a pH of 10, the quantitative precipitation of nickel sulphide should require about 700 min at 40°; however, at 90° the precipitation should be quantitative within about 5 min.

The use of thioacetamide for the precipitation of nickel sulphide appears to have several advantages over the conventional hydrogen sulphide or ammonium sulphide precipitations. When a solution containing nickel nitrate, aqueous ammonia, ammonium chloride and thioacetamide is heated at 90°, a dense, granular precipitate of nickel sulphide is obtained and the clear, colourless supernatant can be easily separated from the precipitate by decantation. Thus, the precipitation of nickel sulphide by thioacetamide avoids the troublesome aspects of the ammonium sulphide precipitation, namely (1): the voluminous precipitate which can be filtered only with great difficulty, (2) the yellowish to black colour of the filtrate caused by the presence of colloidal nickel sulphide, and (3) the lengthy procedure required to coagulate this precipitate. However, when thioacetamide is employed for the precipitation of sulphides and where subsequent operations are to be made with the same solution, the effects of the excess thioacetamide together with its hydrolysis and reaction products must be considered.

It seems possible that thioacetamide could be used to advantage as a substitute for hydrogen or ammonium sulphide in the separation of zinc, nickel and cobalt as sulphides from ammoniacal solutions in which aluminium, chromium and in some cases manganese, are present as tartrate[5] or oxalate[6] complex ions. Before thioacetamide can be employed for such separations, however, it will be necessary to determine experimentally the behaviour of each of the elements involved under the conditions to be used for the separation.

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Zusammenfassung—Die Geschwindigkeit der Fällung von Nickelsulfid aus ammoniakalischen Lösungen mit Thioacetamid wird hauptsächlich durch zwei Reaktionstypen kontrolliert: Reaktionen zwischen den verschiedenen Nickelspezies und Thioacetamid und Reaktionen zwischen Nickel und dem aus der Reaktion zwischen Ammoniak und Thioacetamid stammenden Sulfid; die aus der durch Hydroxylionen katalysierten Hydrolyse von Thioacetamid stammende Sulfidmenge ist relativ klein. Die Geschwindigkeitsausdrücke für die beiden vorherrschenden Prozesse sind

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = \sum_{n=0}^{6} k_n[\mathrm{Ni(NH_3)_n}^{2+}][\mathrm{CH_3CSNH_2}][\mathrm{H^+}]^{-2/3}$$

und

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = k[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2.$$

Résumé—On contrôle la vitesse de précipitation du sulfure de nickel à partir de solutions ammoniacales au moyen de thioacétamide essentiellement par deux types de réactions: réactions entre les différentes espèces du nickel et la thioacétamide, et réactions entre le nickel et le sulfure produit par une réaction thioacétamide-ammoniaque. (Le sulfure produit par l'hydrolyse du thioacétamide catalysée par l'hydroxyde est relativement faible.) Les expressions de la vitesse pour ces deux processus prédominants sont, respectivement:

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = \sum_{n=0}^{6} k_n[\mathrm{Ni(NH_3)_n}^{2+}][\mathrm{CH_3CSNH_2}][\mathrm{H^+}]^{-2/3}$$

et

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = k[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2.$$

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EFFECT OF NUCLEATION ON RATE OF PRECIPITATION OF METAL SULPHIDES BY THIOACETAMIDE*

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Summary—Observations have shown that the number of nuclei formed in thioacetamide precipitations of metal sulphides is usually dependent on the first power of the thioacetamide concentration, and is essentially independent of pH, temperature and metal ion concentration. Under certain conditions a second nucleation process has been observed, in which the number of nuclei formed is proportional to the third power of the thioacetamide concentration, and to the inverse first power of the hydrogen ion concentration. The rate of the *direct reaction* between metal ions and thioacetamide is directly proportional to the number of nuclei formed, and the rate expression is otherwise of zero order in thioacetamide. A partial explanation of this effect is proposed.

INTRODUCTION

IN a previous study[1] of the precipitation of zinc sulphide from ammonia buffers by thioacetamide (TAA), it was observed that the rate of precipitation conformed to the equation

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = K[\mathrm{Zn(II)}][\mathrm{TAA}]\,[\mathrm{H}^+]^{-2/3}.$$

The symbol [Zn(II)] represents the total formal concentration of zinc. Precipitations conforming to equations of this form have been observed previously and the process has been termed the *direct reaction*[2] because the rate equation suggests a reaction between the metal and TAA directly, without an intermediate reaction of TAA to yield sulphide. In the case of zinc, this equation was followed only at relatively low concentrations of TAA; at higher concentrations precipitation proceeded so rapidly that essentially all the zinc precipitated during mixing. The precipitate obtained under these conditions was much more finely divided than that obtained at lower TAA concentrations, suggesting that the phenomenon could be attributed to nucleation processes.

This paper reports a preliminary study of nucleation in the TAA precipitation of several metal sulphides, the bulk of the information having been obtained from systems in which zinc was precipitated from ammonia buffered solutions. The factors affecting nucleation can be most simply elucidated by studying the variation in the number of

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precipitate particles with varying conditions. This variation in the number of particles can be conveniently studied by measuring the turbidity of the precipitate suspension. The ratio of the intensities of the incident and transmitted beam is given by

$$\frac{I}{I_0} = e^{-\tau l}$$

where τ is the turbidity and l is the path length. The relationship between turbidity and particle size and number is complex, but for particles larger than the wavelength of light used, τ is approximately proportional to Nr^2, where N is the number of particles per unit volume and r is the particle radius.[3] Because τ is proportional to the measured absorbance of the solution

$$A \propto Nr^2.$$

The volume of precipitate per unit volume is proportional to Nr^3, and also to C, the moles of metal precipitated per unit volume, so that

$$C \propto Nr^3.$$

Combining these two equations and solving for N, one obtains

$$N \propto A^3/C^2.$$

In the discussion below, the ratio A^3/C^2 will be termed N_{relative}.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used throughout. Stock solutions were prepared and, when necessary, were standardised by conventional methods.

Apparatus

A Bausch and Lomb Spectronic 20 colorimeter was used to measure absorbances. Preliminary investigation revealed that over the range of concentrations employed, the suspensions obtained in this study gave measurements reproducible to within 5–10%.

Procedures

When rates of precipitation were determined, the general procedure followed in previous TAA precipitation studies was employed. The concentration of metal ion in solution at various times was determined by EDTA titration, either of a filtered aliquot of solution or of the precipitate obtained upon filtration of an aliquot.

When the effects of varying the concentrations of the reaction constituents upon the number of nuclei were studied, stock solutions were used to prepare series of four to six reaction solutions, which were identical except for the concentration of the constituent under examination. Except where otherwise noted these precipitations were carried out at room temperature with constant mechanical shaking. After the precipitation had proceeded to a suitable extent, an aliquot of the suspension was taken for the colorimetric determination of turbidity. Simultaneously, another aliquot was analysed to determine the amount of material precipitated. From this information, A^3/C^2, proportional to N, was computed.

RESULTS AND DISCUSSION

Effect of thioacetamide concentration on number of zinc sulphide nuclei

The effect of TAA concentration on the number of particles formed was studied in a series of experiments in which varying amounts of solid TAA were added to stock buffer solutions and agitated thoroughly for 10 sec, after which a fixed volume of zinc nitrate solution was added to each. The relative number of particles formed in each precipitating solution was then determined as outlined above. Because the method of mixing the components of the reacting system affects the number of particles formed, the above method was followed closely except where otherwise noted. Fig. 1 shows the results of these experiments in a plot of log N *vs.* log ([TAA] × 10^2). It can be seen that at low concentrations of TAA, N is directly proportional to [TAA], and at high concentrations N is proportional to $[\mathrm{TAA}]^3$. The two nucleation processes distinguished in this way will subsequently be referred to as the *first order nucleation* and the *third order nucleation*, and will be discussed separately.

First order nucleation process

Additional experiments similar to those outlined above on the precipitation of nickel sulphide from ammonia buffers, and of zinc, cadmium and nickel sulphides from formate buffers (pH about 5) showed that the first order nucleation is predominant. Further experiments showed that the number of particles formed by this process is independent of the concentration of metal ion, of ammonia, of pH and of temperature. These results indicate that nucleation was taking place on insoluble impurities in the TAA. In such cases the number of nuclei formed by this process should then depend only on the number of impurity particles, and hence on the quantity of a given sample of TAA and should be independent of other reaction conditions.

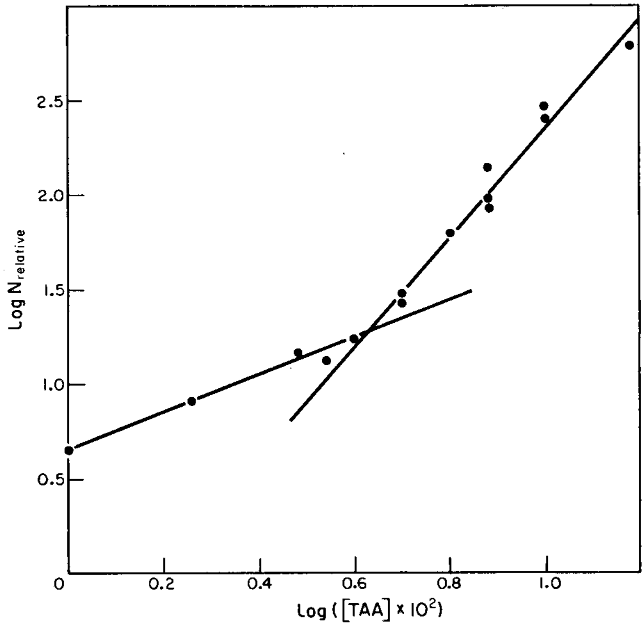

FIG. 1.—Effect of thioacetamide concentration on number of zinc sulphide nuclei (initial conditions: [Zn(II)] = 0·010*VF*, $NH_{3_{total}}$ = 0·115*VF*, NH_4NO_3 = 0·230*VF*, pH = 9·02, temperature *ca.* 25°)

This hypothesis was tested by carrying out the following experiments:

(1) Six different samples of solid TAA, from four commercial sources, were employed to precipitate zinc sulphide. Three of the samples were obtained from the same source and differed only in lot number: these three samples produced an essentially constant number of particles. The samples from the other source yielded from two to four times as many particles as did the first set of samples. These results indicate that

the number of nucleating particles present in any sample of TAA depends upon the prior history of the TAA.

(2) The variation of N with TAA concentration was observed, using a TAA solution which had been filtered through a membrane filter (pore size 100 mμ), and for comparison, an unfiltered TAA solution. The results, shown in Fig. 2, indicate that filtration inhibits the first order nucleation, and only third order nucleation is observed.

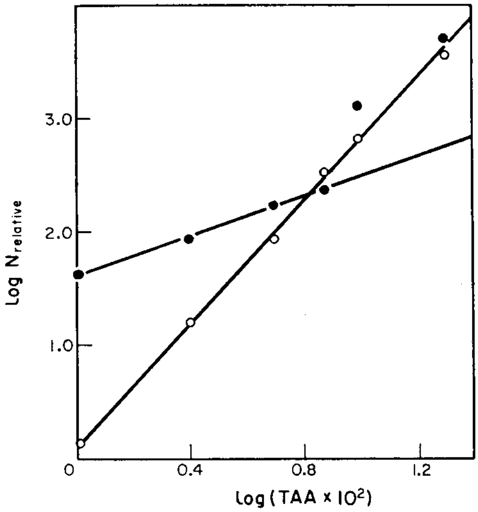

FIG. 2.—Effect of filtration on number of zinc sulphide nuclei [initial conditions: [Zn(II)] = 0·0050 VF, NH_{3total} = 0·099 VF, NH_4NO_3 = 0·040 VF, pH = 9, temperature *ca.* 25° (room temperature)].

● TAA unfiltered, ○ TAA filtered.

Third order nucleation process

A previous study of the TAA precipitation of nickel sulphide from ammonia buffered solution[4] did not reveal the very rapid precipitation observed in the analogous precipitation of zinc sulphide, nor had the rapid precipitation been obtained in the precipitation of zinc sulphide from acidic solutions.[5] Consequently, experiments were carried out to determine whether the third order nucleation process related to this rapid precipitation is a specific phenomenon occurring only with zinc ammines, or whether it occurs more generally.

Accordingly, the variation of N with TAA concentration was studied in the precipitation of nickel sulphide from an ammonia buffer (pH) 9, with TAA concentrations from 0·074 VF to 1·00 VF. These experiments show that a third order nucleation does take place, but not to a significant extent unless the TAA concentration is above about 0·6 VF. In the previously noted studies of the precipitation of zinc sulphide from ammonia buffers, the third order nucleation became predominant at TAA concentrations above about 0·06 VF.

In experiments in which zinc sulphide was precipitated from formate buffers, pH about 5, only first order nucleation was observed, even at TAA concentrations as high as 1·1 VF. When the first order nucleation was inhibited by prior filtration of the TAA solution through a membrane filter, first order nucleation was not observed, and the third order process prevailed down to the lowest TAA concentration employed, 0·01 *VF*. Analogous experiments with filtered TAA have not been carried out with other metals.

Precipitation of zinc sulphide from ammoniacal solutions was used to study the dependence of the third order nucleation process on concentrations of the reaction constituents. The number of particles formed at a given concentration of TAA was independent of the concentrations of zinc and ammonia, but was inversely proportional to the concentration of hydrogen ion over the pH range 8·6 to 10·2. The temperature dependence of the third order nucleation was not studied. Current concepts of homogeneous nucleation require some metal ion dependence; therefore, this process also appears to be heterogeneous, possibly involving particles different in nature from those responsible for the first order process.

Nature of direct reaction between thioacetamide and metal ions

The precipitation of metal sulphides by TAA in general follows one or both of two reaction paths. The TAA may react to give sulphide, which then precipitates the metal ion; in previous experiments the rate of this precipitation has been found to be the same as the rate of formation of sulphide. The second process, the *direct reaction* previously discussed, does not involve prior formation of sulphide; the rate of this precipitation reaction has been found to conform to the following equation for a number of dipositive metals:

$$-\frac{d[M]}{dt} = k\,[M][TAA]\,[H^+]^{-1}\;{}^{2} \tag{1}$$

Mechanistically, the rate of a precipitation is fixed by the rate at which the precipitating ions can diffuse to the surface of the precipitate particles, or by the rate at which the ions at the surface are incorporated into the particles, *i.e.*, the over-all rate of precipitation is dependent upon either a diffusion process or an interface process, or both. In certain cases of precipitations from homogeneous solution, the rates of these processes are limited by the rate at which precipitant is generated, so that the over-all rate of the precipitation will be controlled by the rate of generation of precipitant, with deviations only at the beginning and end of the precipitation, where the concentration of one of the precipitating ions is quite small.

Because the direct reaction does not involve prior formation of sulphide, equation (1) must describe either a diffusion process or an interface process. Diffusion-limited precipitation cannot be described by a rate equation of the form of equation (1);[6] therefore, the observed kinetics of the direct reaction can be attributed to an interfacial process. The rate at which an interfacial reaction proceeds depends upon the area of the interface. In a precipitating system this interfacial area is the product of the number of particles and the area per particle. Although the actual surface area per particle increases as precipitation proceeds, the effective growth area of the particles need not increase; it has frequently been observed[7] that each growing particle apparently contains only a fixed number of sites which are active in growth. In this case the precipitation rate will depend only on the number of growing particles in the system, and not on the surface area.

Equation (1), with slight modification, fits this model, where the number of sites is proportional to the number of particles, and the number of particles is that number formed by the first order nucleation process, and so is proportional to the TAA concentration. Equation (1) may now be rewritten

$$-\frac{d[M]}{dt} = k\,[TAA]_0[M]\,[H^+]^{-1/2} \tag{2}$$

where $[TAA]_0$, the original TAA concentration, is directly proportional to the number of active growth sites. This modification of the observed rate equation predicts that the direct reaction is kinetically of zero order in TAA, *i.e.*, that the rate of the precipitation will not decrease as TAA is consumed by the reaction.

In previous studies[1,2,4,5] of the direct reaction where equation (1) was observed, TAA was present in large excess. Thus, the concentration of TAA remained essentially constant during the precipitation, and the dependence of the precipitation rate on TAA concentration was determined by varying the initial concentration of TAA, a procedure which also varies the number of nuclei, and thus cannot determine whether the precipitation is described by equation (1) or (2). Experiments involving the precipitation of cadmium sulphide from acidic solution, and of zinc sulphide from ammoniacal solution, were carried out, and the results indicate that the precipitation is described by equation (2). In these experiments, the metal ion and TAA were present in equivalent amounts, or the metal was present in excess. Results from one of these experiments are presented in Table I.

TABLE I.—DEPENDENCE OF RATE OF PRECIPITATION OF CADMIUM SULPHIDE ON CONCENTRATION OF THIOACETAMIDE IN SOLUTION

Time, *min*	CdS precipitated, *mole. litre*$^{-1}$	k_1,[a] *litre. mole*$^{-1}$*. min*$^{-1}$	k_2,[b] *litre. mole*$^{-1}$*. min*$^{-1}$
6	0·0020	0·028	0·029
24	0·0077	0·027	0·033
34	0·0101	0·026	0·033
49	0·0162	0·028	0·048
60	0·0190	0·026	0·055
72	0·0230	0·027	0·107
89	0·0234	—	—

(Initial conditions: $[Cd^{2+}] = 0{\cdot}50\,VM$, TAA $= 0{\cdot}0235\,VF$,
pH = 5·78 (formate buffer), temperature = 80°)

[a] Calculated from $-\frac{d[Cd^{2+}]}{dt} = (k_1[TAA]_0)[Cd^{2+}]$.

[b] Calculated from $-\frac{d[Cd^{2+}]}{dt} = k_2[TAA][Cd^{2+}]$.

In order to form metal sulphide by the direct reaction, a reaction between the metal ion and TAA must take place. Because, according to equation (2), the solution concentration of TAA does not affect the rate, the metal-TAA reaction must take place under conditions such that the TAA concentration is constant. This will be the case when TAA is present as an adsorbed layer on the precipitate, provided that a large fraction of the available adsorption sites is occupied by TAA even at low TAA concentrations.

It is now possible to propose the following process to describe the TAA precipitation of metal sulphides by the direct reaction. Nucleation takes place on particles introduced into the system with the thioacetamide, the number of such particles usually being directly proportional to the quantity of thioacetamide added. Each nucleus formed in this way adsorbs TAA until essentially all its adsorption sites are filled. Metal ions diffuse rapidly to the surface of the particles, but are incorporated into the precipitate only slowly, by reaction with the adsorbed TAA molecules. Such a reaction can occur only at specific areas of the particle surface, each particle having a fixed number of these active growth areas. The role of hydrogen ion in the direct reaction is not explained by this process. The inverse half order hydrogen ion dependence of the direct reaction may indicate either a pH-sensitive adsorption of the metal on TAA or an effect of pH on the number of active growth areas.

Zusammenfassung—Es wurde beobachtet, daß die Anzahl der bei Thioacetamidfällungen von Metallsulfiden gebildeten Keime im allgemeinen von der Thioacetamidkonzentration linear abhängt und im großen und ganzen von pH, Temperatur und Metallionenkonzentration unabhängig ist. Unter bestimmten Bedingungen wurde ein zweiter Keimbildungsprozeß beobachtet, bei dem die Keimzahl proportional zur dritten Potenz der Thioacetamidkonzentration und umgekehrt proportional zur ersten Potenz der Wasserstoffionenkonzentration ist. Die Geschwindigkeit der "direkten Reaktion" zwischen Metallionen und Thioacetamid ist direkt proportional zur Keimzahl; im übrigen ist der Geschwindigkeitsausdruck nullter Ordnung bezüglich Thioacetamid. Eine teilweise Erklärung für diesen Effekt wird vorgeschlagen.

Résumé—Des observations ont montré que le nombre de germes formés dans les précipitations de sulfures métalliques au moyen de thioacétamide dépend habituellement de la puissance première de la concentration en thioacétamide, et est essentiellement indépendant du pH, de la température et de la concentration en ion métallique. Dans certaines conditions, on a observé un second processus d'amorçage, dans lequel le nombre de germes formés est proportionnel à la puissance troisième de la concentration en thioacétamide, et inversement proportionnel à la puissance première de la concentration en ion hydrogène. La vitesse de la "réaction directe" entre les ions métalliques et le thioacétamide est directement proportionnelle au nombre de germes formés, et l'équation de vitesse est autrement d'ordre zéro dans le thioacétamide. On propose une explication partielle de cet effet.

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SELEKTIVE TRENNUNG VON SELEN(IV) DURCH EXTRAKTION MIT METHYLÄTHYLKETON

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Zusammenfassung—Selen(IV) wird mit Methyläthylketon in salzsaurem Medium extrahiert und hierbei die optimale Acidität bestimmt, bei der die Extraktion vollständig ist. Ferner wird die Assoziationskinetik der Selenchloridkomplexe mit Methyläthylketon sowie die Extraktionskinetik des Assoziats mit Chloroform untersucht. Hierbei wird auf die Möglichkeit hingewiesen, Selen in Gegenwart zahlreicher, in beträchtlicheren Mengen vorhandener Stoffe, darunter auch Tellur, durch Extraktion zu trennen. Bestimmt wurde auch der Selengehalt in Kupferkonzentraten. Abschliessend folgen statistische Bearbeitung der Ergebnisse und Bewertung der Genauigkeit der Methode.

DIE Trennung des Selens von anderen Elementen ist in der analytischen Praxis stets mit erheblichen Schwierigkeiten verknüpft. Ein Teil der üblichen Methoden[1–6] beruh auf der Reduktion von Selen(IV) zu Elementarselen, das mit Tellur oder einem anderen geeigneten Fällungsmittel mit zur Fällung gebracht wird. Diese Methoden können jedoch die vollständige Trennung von Selen nicht gewährleisten. Anderen Methodent liegt die Extraktion zugrunde. Zur Anwendung gelangen unterschiedliche Extraktionsmittel wie Triphenylarsoniumchlorid,[7] *N*-Dodecyltrioktylmethylamin, Tribenzylamin,[8] Ditizon,[9] Methylisobutylketon,[10]Tributylphosphat,[11] Diäthyldithiophosphorsäure,[12] Triphenylblei,[13] Tri-*N*-oktylphosphinoxyd,[14] 3,3′-Diaminobenzidin[15–20] u.a. Auch diese Methoden vermögen nicht eine ausreichend vollständige, selektive und anspruchslose Trennung des Selens von anderen Elementen zu verwirklichen.

In der vorliegenden Arbeit weisen wir auf einen Weg der Selenextraktion hin, der den erwähnten Erfordernissen in weitgehendem Masse Rechnung trägt.

EXPERIMENTELLER TEIL

Nachdem wir eine Reihe von Extraktionsmitteln auf deren Wirksamkeit bei Selen geprüft hatten, entschieden wir uns für das Methyläthylketon, das uns am geeignetesten erschien. Es stellte sich nämlich heraus, dass sowohl reines Methyläthylketon als auch seine stark verdünnte Chloroformlösung extraktionsfähig sind.

Man könnte erwarten, dass die Extraktion nach dem Oxonium-Mechanismus vor sich geht. In diesem Fall würden die günstigsten Extraktionsbedingungen dann eintreten, wenn Selen in einem negativ geladenen Komplex vorliegt.

In salzsaurem Medium hat man die Bildung von Selen(IV)-chlorid-Komplexen beobachtet.[21–27] Nach Petzold[28] stellen sich je nach der Konzentration der Salzsäure nachstehende Gleichgewichte ein:

$$H_2SeO_3 + 4HCl \rightleftharpoons SeCl_4 + 3H_2O$$
$$SeCl_4 + 2HCl \rightleftharpoons H_2SeCl_6.$$

Durch spektrophotometrische Untersuchung der Komplexbildung im System Selen(IV)/Chlorionen stellten Babko und Mitjurewa[29] fest, dass bei 4,5M HCl die Bildung von Chloridkomplexen einsetzt, denen die Autoren die wahrscheinliche Zusammensetzung $Se(OH)_2Cl_2$ zuschreiben.

Untersuchungen über den Einfluss der Acidität auf die Extraktion von Selen

Zu 1 ml einer Lösung, die 100 μg Se enthält, geben wir jeweils 9 ml Salzsäure von unterschiedlicher Normalität und anschliessend 0,5 ml Methyläthylketon hinzu. Die Lösung wird kräftig geschüttelt, 10 Min. liegen gelassen und nachher mit 10 ml Chloroform extrahiert. Abb. 1 veranschaulicht den Zusammenhang zwischen Extraktionsgrad und Acidität. Man sieht, dass die Extraktion bei 4,5M HCl merklich zunimmt, was mit den Untersuchungsergebnissen von Babko und Mitarbeitern im Einklang steht. Bei 6,5M HCl ist die Extraktion des Selens nahezu vollständig. Rückschlüsse auf die Selenverteilung konnten wir ziehen, indem, wir seinen Gehalt in beiden Phasen bestimmten. Zu diesem Zweck bedienten wir uns der photometrischen Methode, der die Messung der optischen Dichte einer Kolloidlösung zugrundeliegt, die durch Reduktion von Selen(IV) mit Zinn(II)-chlorid in Gegenwart von Wismutnitrat und Gelatine gewonnen wurde.

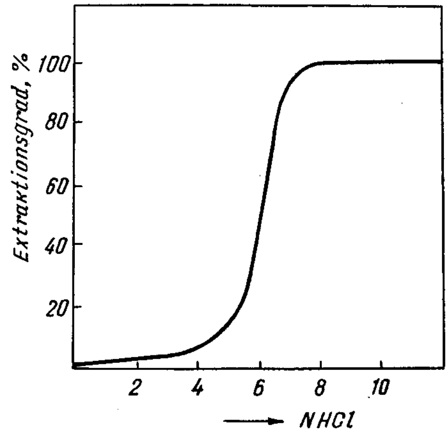

ABB. 1

Untersuchung der Assoziations- und Extraktionskinetik

Unter Voraussetzung des vermutlichen Oxonium-Mechanismus der Extraktion und Berücksichtigung des Umstandes, dass Methyläthylketon sich ziemlich leicht in Wasser löst, hielten wir es für zweckmässig, zunächst einmal die Assozierung des Selen(IV)-chlorid-komplexes mit dem Methyläthylketon in salzsaurem Medium durchzuführen und dann das erhaltene Assoziat mit Chloroform zu extrahieren. Die Angaben über die Assoziationskinetik sind aus Abb. 2 zu ersehen. Demnach

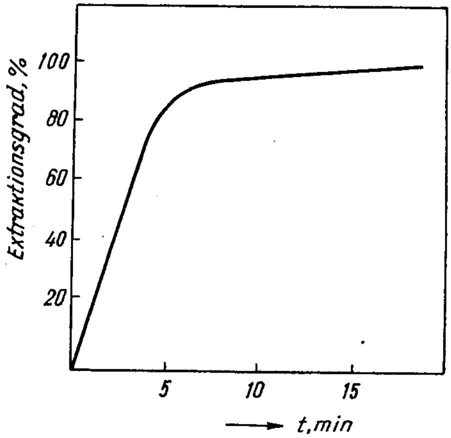

ABB. 2

ist die Geschwindigkeit der Assoziation nitch sehr gross. Beträgt die Konzentration des Selens $1{,}2 \cdot 10^{-4}$M und die des Methyläthylketons 0,35M, so vollzieht sich die vollständige Assozierung innerhalb von 15 Min. Die Extraktion mit Chloroform geht viel schneller vor sich.

Untersuchungen über die Rückextraktion von Selen

Zwecks analytischer Anwendung der Methode ist es von Belang, einen Weg zur quantitativen Rückextraktion des Selens zu suchen. Versuchsweise wurden zwar zahlreiche einschlägige Mittel angewendet, doch ohne Erfolg. Schliesslich wurde diese Frage in nachstehend geschilderter Weise gelöst. Der Chloroformauszug wurde in einem Messkolben gesammelt und nach Zugabe von 2 ml Wasser und 0,5 ml konz. Salpetersäure im Wasserbad erhitzt. Es entwich zuerst das Chloroform, dann trat die Zersetzung des Methyläthylketons ein. Man erhitzt bis zum Aufhören der Gasentwicklung und völligen Entfärben der Lösung. Eigens angestellte Versuche ergaben, dass bei diesen Umsetzungen kein Verlust an Selen zu verzeichnen war.

Untersuchung über die Störende Wirkung anderer Stoffe

Konzentrationen bis 0,6M für die Schwefelsäure und 0,5M für die Salpetersäure stören die Extraktion nicht. Diese wird praktisch nicht gestört auch von vielen anderen, in den Auszug nicht übergehenden Stoffen, wenn diese in nachstehend angegebenen Mengen (Tabelle I) vorhanden sind.

TABELLE I

Fe(III)	50 mg	Bi(III)	50 mg	Sb(III)	50 mg
Al(III)	50 mg	Ni(II)	50 mg	Sb(V)	50 mg
Cu(II)	100 mg	Co(II)	50 mg	Au(III)	1,5 mg
Mn(II)	50 mg	V(V)	30 mg	Mo(VI)	50 mg
Cd(II)	50 mg	As(III)	1 mg	Mg(II)	50 mg
Zn(II)	50 mg	As(V)	50 mg	Te(IV)	50 mg

Auch geringe Mengen von Tl, In, Ga, Ge, W und Th stören die Extraktion nicht, während das Vorhandensein starker Oxydationsmittel, vermutlich durch Oxydation von Selen(IV) zu Selen(VI), störend wirkt. Ist die Menge der Begleitstoffe grösser als die in Tab. I angegebene, so werden sie teilweise mit extrahiert und manche von ihnen wirken dann störend bei der weiteren Bestimmung des Selens. In diesem Falle wird empfohlen, die organische Phase mit 3–4 ml gesätiger lösung von Natrium Chlorid bzw mit derselben Menge von 7M HCl zurück zu extrahieren.

Die Klärung der mit dem Mechanismus der Extraktion verknüpften Fragen der Komplexbildungs- und Assoziierungsprozesse sowie der selektiven Extraktionswirkung des Methyläthylketons in Chloroform soll unseren nachträglichen Forschungen vorbehalten sein.

Anwendung der Methode

Erforderliche Reagenzien

Standartlösung von Selen. Man löst 1,4050 g über Phosphorpentoxyd getrocknetes Selenoxyd in Wasser bis auf 1 L. Diese Lösung enthält 1000 μg Se/ml. Durch entsprechende Verdünnung entstehen Lösungen, die 100 bzw. 10 μg Se/ml enthalten.

Zinn(II)-chlorid, 25%ige Lösung. Man löst 125 g $SnCl_2$ in 100 ml konz. HCl, erwärmt im Wasserbad bis zum Klarwerden und verdünnt dann mit Wasser auf 500 ml.

Wismut(III)-nitrat, 1%ige Lösung. 5 g $Bi(NO_3)_3$ wird in 150 bis 200 ml Wasser gelöst; man säuert dann mit Salpetersäure an bis zum Klarwerden der Lösung und verdünnt mit Wasser auf 500 ml.

Gelatine, 0,5%ige Lösung. 1 g reiner Gelatine wird in 100 ml heissem Wasser gelöst, mit 1 ml konz. HCl angesäuert und auf 200 ml verdünnt.

Konzentrierte Salz-, Schwefel- und Salpetersäure
Methyläthylketon p.a.[a]
Chloroform p.a.

Analysengang

0,5 bis 3,0 g des Probegutes (Kupfer- und Bleikonzentrate, Blei/Silber-Legierung, schwarzes Kupfer u.a.) werden in 5 bis 15 ml konz. Salpetersäure gelöst. Man erhitzt und dampft die Lösung auf einige ml ein. Nach Zagabe von 2 ml konz. Schwefelsäure wird weiter erhitzt bis zur Entwicklung von Dämpfen (SO_3). Man Kühlt ab, setzt 3 bis 4 ml Wasser hinzu und erwärmt abermals bis zur

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[a] Methyläthylketon wird bei der trockenen Holzdestillation gewonnen und ist deshalb oft gelb gefärbt. Dann muss es abdestilliert und als farbloses Produkt gesammelt werden.

Zersetzung der Schwefelsäure. Der Rückstand wird mit 20 ml 7M HCl versetzt und filtriert. Das Filtrat wird in einem Messkolben von 50 ml gesammelt. Den Niederschlag wäscht man mit derselben Säure aus und den Kolben füllt man bis zur Marke. 10 ml der Lösung bringt man in einen Scheidetrichter, setzt 0,3 ml Methyläthylketon hinzu, schüttelt und lässt dann die Lösung 15 Min. lang liegen. Nachher wird 3 Min. lang mit 10 ml Chloroform extrahiert. Die organische Phase wird in einem 50 ml-Messkolben gesammelt, die wässerige Phase mit 2 bis 3 ml Chloroform gewaschen und dann in denselben Kolben gebracht. Nach Zugabe von 2 ml Wasser und 0,5 ml konz.Salpetersäure erwärmt man vorsichtig im Wasserbad bis zur Entfernung des Chloroforms; die Erwärmung wird dann längere Zeit fortgesetzt bis zur völligen Zersetzung des Ketons. In die farblose Lösung bringt man 20 ml Wasser, 6 ml konz.Salzsäure, 1 ml Wismutnitratlösung und verdünnt dann mit Wasser auf etwa 40 ml. Nach Zusatz von 0,5 ml Zinn(II)-chlorid-Lösung wird energisch gerührt, worauf die Lösung 15 Min. lang stehen gelassen wird. Nachher setzt man 4 ml Gelatinelösung hinzu, füllt mit Wasser bis zum Strich und photometriert bei $\lambda = 450$ mμ. Man benutzt eine Küvette mit Stärke der absorbierenden Schicht 5 cm. Als Bezugslösung wird Wasser verwendet.

Die Bestimmung des Selengehalts erfolgt nach vorgezeichneter Standardkurve. Zu dem Zweck werden 10 bis 100 μg Selen extrahiert. Der Auszug wird in vorstehend beschriebener Weise aufgearbeitet und die optische Dichte der jeweiligen Lösung bestimmt.

Statistische Bewertung der Genauigkeit der Methode

Die Bewertung der Genauigkeit der Methode erfolgt durch statistische Bearbeitung der Ergebnisse, die wir bei der Bestimmung von 30 μg Selen unter reinen Bedingungen und bei der Ermittlung des Selengehalts im Kupferkonzentrat erhielten.*

$$\text{I}\quad 30\,\mu\text{g Se}\,.\ \text{N} = 10,\ \text{E} = 0{,}181,\ \text{s} = 0{,}0063,\ \text{v} = \frac{\text{S}}{\text{E}}\,.\,100 = 3{,}46\%.$$

$$\text{II Kupferkonzentrat. N} = 10,\ \bar{\text{x}} = 225{,}7\ \text{g Se/t},\ \text{s} = 3{,}38,\ \text{v} = \frac{\text{s}}{\bar{\text{x}}}\,.\,100 \doteq 1{,}59\%.$$

Summary—Selenium(IV) may be extracted by methyl ethyl ketone in a hydrochloric acid medium. The optimum acidity for the extraction has been determined. The kinetics of the association of the selenium chloride complex with methyl ethyl ketone, and of the extraction of the association complex by chloroform, have been examined. In consequence it is possible to separate selenium from considerable amounts of other materials, including tellurium, by extraction. The selenium content of copper concentrates can be determined. A statistical examination of the results, and an estimate of the accuracy of the method are included.

Résumé—On peut extraire le sélénium(IV) par la méthyl-éthyl-cétone en milieu acide chlorhydrique. On a déterminé l'acidité optimale pour l'extraction. On a examiné la cinétique de l'association du complexe chlorure de sélénium avec la méthyl-éthyl-cétone, et celle de l'extraction du complexe d'association par le chloroforme. En conséquence, il est possible de séparer le sélénium–quantités considérables d'autres produits, y compris le tellurium, par extraction. On peut déterminer la teneur en sélénium de concentrats de cuivre. On a inclus dans cette étude un examen statistique des résultats, et une estimation de la précision de la méthode.

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* Die Rückextraktion des Selens aus der organischen Phase mit Wasser und verdünnter Lösung von Salzsäure haben wir zwar geprüft doch mit negativen Ergebnissen. Das läßt sich durch die Irreversibilität der Prozesse der Komplexbildung und Assoziierung erklären. Nachträgliche Untersuchungen zeigten daß das Assoziat zwischen dem Chloridkomplex des Selens und dem Methyläthylketon ziemlich stabil ist. Hierzu kommt es, daß die Assoziation durch die Salzsäure insofern gefördert wird, als sie die Dielektrizitätskonstante des Mediums herabsetz. In dieser Hinsicht ist das Methyläthylketon maßgeblicher, das in der Wasserphase in weitgehendem Maße löslich ist.

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AMPEROMETRY WITH TWO POLARISABLE ELECTRODES—III*

CHELOMETRIC DETERMINATION OF IRON(III) USING AN INDICATION SYSTEM OF TWO CARBON ELECTRODES

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Summary—Two carbon (graphite) electrodes have been used for indicating the end-point in the biamperometric titration of iron(III). Satisfactory results are obtained over a wide range of applied potentials. The absolute current values are related linearly to the values of the applied potential. At a potential of 0·6–2·0 V the current differences during the titration are from several μA to ten times these values. The influence of pH, applied potential and temperature on the titration have been studied; the effect of interfering elements has been investigated. Under optimal conditions the determination is highly selective and accurate. It is possible to determine 1–150 mg of iron(III).

IN a preliminary communication,[1] the possibility of using two carbon (graphite) electrodes for biamperometric detection of the end-point in titrations with EDTA was mentioned. Previously, the carbon electrode had been used as an indicator electrode in potentiometric and amperometric titrations[2] and also in polarography.[4] For biamperometric titrations with two polarisable electrodes ("dead-stop" method) an electrode system of two carbon electrodes has not yet been applied.[5]

In the present paper the results are reported of a study of the conditions for the biamperometric titration of iron(III) with EDTA using an indication system of two carbon electrodes. Recently, this titration was investigated with an electrode system of two platinum electrodes.[6]

EXPERIMENTAL

Reagents

Unless otherwise stated, all solutions were prepared from reagent-grade chemicals.

Foreign ion solutions. Solutions of Ni^{2+}, Cu^{2+}, Th^{4+}, Zr^{4+}, Al^{3+}, Ti^{4+}, UO_2^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Hg^{2+}, Pb^{2+}, Mg^{2+} and Sn^{2+} were prepared from salts soluble in water.

Buffer solutions (pH 1–4·2). Prepared from 1*M* trichloracetic acid (pH 1·1–1·5), monochloracetic acid (pH 2–2·8) and formic acid (pH 4·2–5·3) by neutralisation with aqueous ammonia under potentiometric control of pH with a glass electrode.

Standard iron(III) *solution.* Prepared by dissolution of behanite (99·8% Fe) in a minimum amount of hydrochloric acid (1:1) and a little 30% hydrogen peroxide. After dissolution, the hydrogen peroxide was decomposed and the cooled solution diluted with redistilled water to 1000 ml. The amount of iron in this solution was determined gravimetrically [1 ml ≡ 1·027 mg of Fe(III)], and the value checked regularly.

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* Part II: see reference 7.

0·05M EDTA solution. Prepared by dissolution of 33·22 g of Chelaton 3 (Lachema, Brno, Czechoslavakia) and dilution to 2000 ml with redistilled water. The titre was determined by titration against standard lead nitrate solution with Xylenol Orange as indicator.[8]

Apparatus

For indication of the end-point a "dead-stop" instrument was used.[9] Two spectrographic carbon electrodes of 5-mm diameter (KABLO, Bratislava, Czechoslovakia, 99·99% carbon) were used. They were placed in glass tubes and covered with plastic (dentacryle) so that only 10 mm of their length remained exposed (Fig. 1). When not in use, the electrodes were kept immersed in water.

The pH was measured with a glass electrode and an electronic pH meter Multoscop III (Laboratorní potřeby, Prague, Czechoslovakia). Polarographic measurements were carried out with a polarograph LP 55 (Laboratorní přístroje, Prague, Czechoslovakia).

Procedure

The chosen amount of iron(III) was diluted to about 150 ml with redistilled water in a 250-ml beaker and the pH adjusted under potentiometric control with hydrochloric acid or sodium hydroxide or with 15 ml of a suitable 1*M* buffer solution. The titrations were carried out at pH 1·5–2·0 in unbuffered solution at 20° with intensive stirring (1600 rpm) using 0·05*M* EDTA solution. All titrations were started 2–3 min after inserting the electrodes into the solution. During this time the "equilibrium" of the electrode reactions was established. The change of current was read after each addition of titrant during the titration. The stabilisation of current values is satisfactory mainly at the end-point and after it.

All data given in this paper are the arithmetical mean of three determinations.

RESULTS AND DISCUSSION

Influence of pH

It is well known that the chelometric titration of iron(III) takes place in a relatively acidic medium. From the point of view of selectivity, the optimum condition for this titration is, of course, the maximum possible acidity. The influence of pH on the biamperometric titration of iron(III) was studied in buffered (Fig. 2) and unbuffered (Fig. 3) media. Titration proceeds satisfactorily at pH 1·1–2·5 in the unbuffered medium and pH 1·1–4·2 in the buffered solution. At other values of pH, detection of the end-point is impossible.

Influence of applied potential

The influence of the applied potential was investigated over the range 0·6–2·0 V (Fig. 4). Satisfactory results can be obtained even at an applied potential lower than 0·6 V, but in this case the amperometer used must be more sensitive. This phenomenon had previously been encountered in the biamperometric titration of thallium(III).[7] For measurements in the range 0·6–2·2 V of applied potential, a microammeter with full-scale deflection of 0–750 μA was used. The mean relative error of the determination of 15 mg of iron(III) was ±0·1%.

Influence of temperature

Although the titration proceeds very well at room temperature, the influence of temperature was studied. It was found that at higher temperatures the stabilisation of current at the beginning of the titration is somewhat faster; no other differences were found.

"Passivation" of electrodes

The aim of the following experiments was to find the appropriate influence of the products of the electrode reactions. These products can cover the surface of the electrode and change the indicator properties of the electrode couple. From this point of

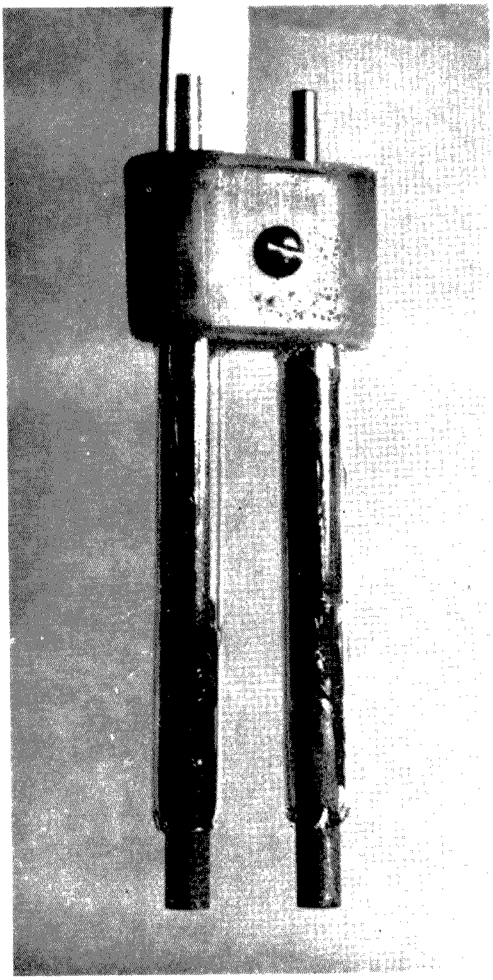

FIG. 1.—Carbon (graphite) indicator electrodes for biamperometric titration of iron(III).

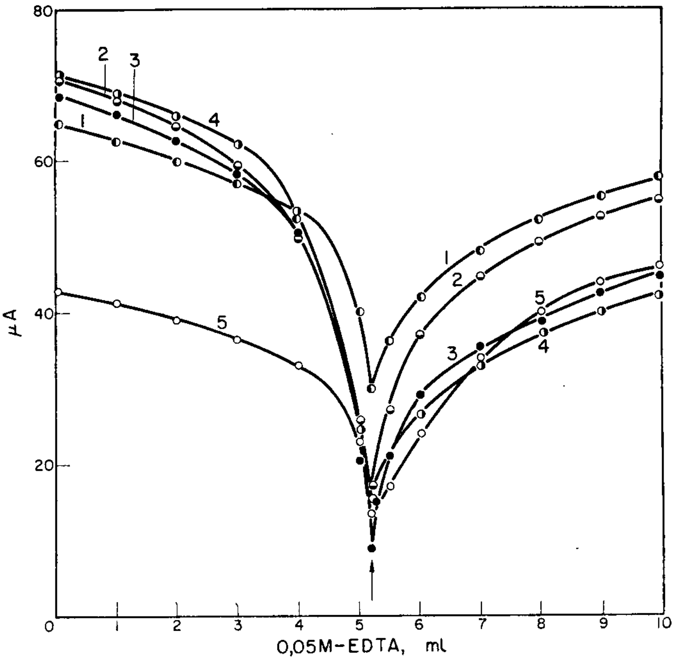

FIG. 2.—Influence of pH on the titration curves in buffered solution:— *1*—pH 1·1; *2*—1·5; *3*—2·0; *4*—2·8; *5*—4·2. [15·41 mg of Fe(III); total volume: 150 ml; temperature: 20°; applied potential: 1·0 V.]

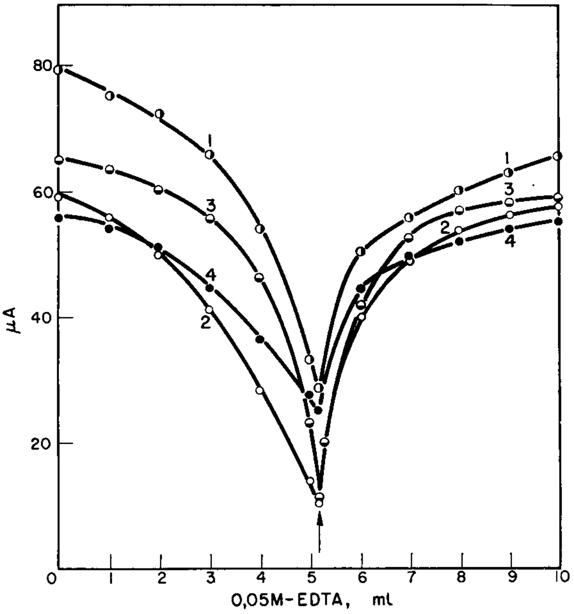

FIG. 3.—Influence of pH on the titration curves in unbuffered solution:— *1*—pH 1·1; *2*—1·5; *3*—2·0; *4*—2·5. [15·41 mg of Fe(III); total volume: 150 ml; temperature: 20°; applied potential: 1·0 V.]

view, 50 determinations of iron were carried out under identical conditions over 24 hr. After each titration the electrodes were only washed with distilled water. Fig. 5 shows the spread of the 50 titration curves. The relative error in these titrations was not greater than ±0·2%.

Subsequently, attention was paid to the decrease of the current at the moment when the electrodes were inserted into the titration solution. In Fig. 6 is given the dependence of the current on time, where the start of the time axis is the time of inserting the electrodes. Curve 1 shows this dependence for the system of two carbon electrodes: in this case the electrodes were first soaked for 144 hr in $0{\cdot}1M$ potassium chloride solution. Curve 2 shows the dependence when the electrodes were first soaked for the same time in distilled water. These curves show that saturation of the carbon electrodes with potassium chloride has practically no influence on stabilisation of the current. In both cases, after 5 min, only a small decrease of the current occurs. For analytical application it is enough to wait 2–3 min after inserting the electrodes

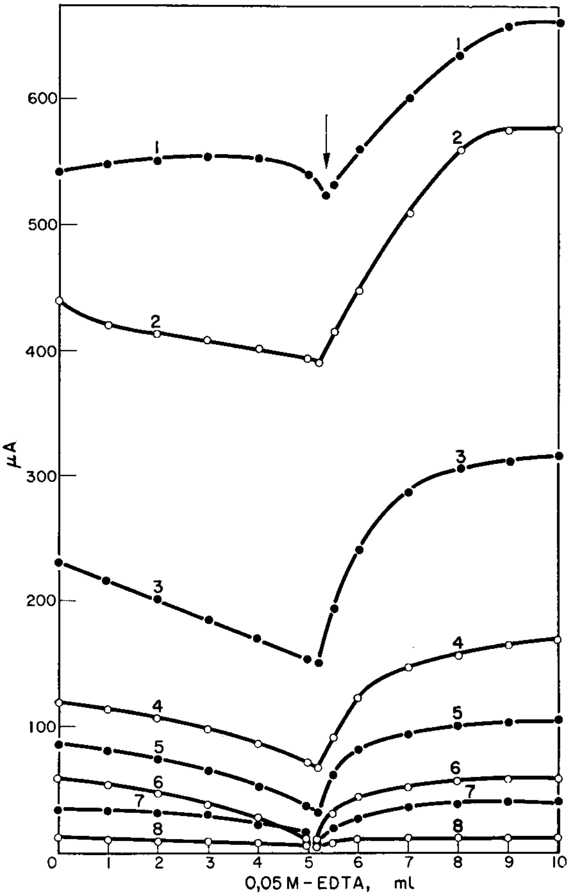

FIG. 4.—Influence of applied potential on the titration curves:— *1*—2·0 V; *2*—1·8 V; *3*—1·6 V; *4*—1·4 V; *5*—1·2 V; *6*—1·0 V; *7*—0·8 V; *8*—0·6 V. [15·41 mg of Fe(III); total volume: 150 ml; pH: 1·7 (unbuffered); temperature: 20°].

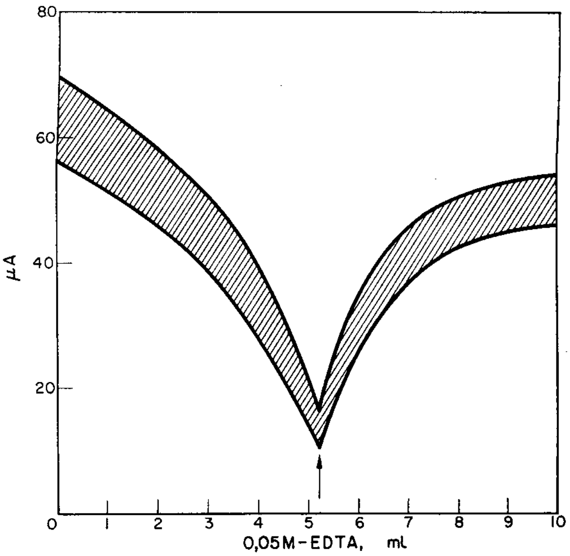

FIG. 5.—Spread of titration curves in 50 titrations [15·41 mg of Fe(III); total volume: 150–180 ml; temperature: 20°; pH: 1·5–2·0; theoretical consumption: 5·20 ml of 0·05*M* EDTA; applied potential: 1·0 V].

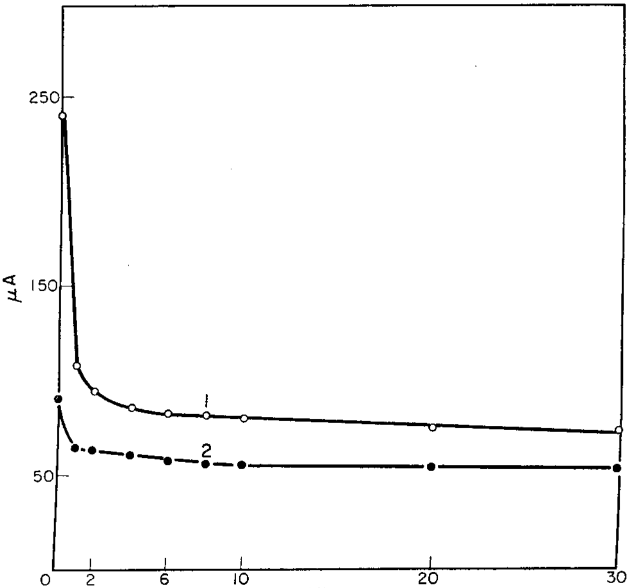

FIG. 6.—Current-time curves at the stabilisation of current values:— *1*—0·1*M* KCl; *2*—distilled water. [15·41 mg of Fe(III); total volume: 150 ml; pH: 1·7 (unbuffered); temperature: 20°; applied potential: 1·0 V].

into the titration solution. However, when one starts the titration immediately, no great differences in the course of the titration are found.

The decrease of the current just after the potential is applied is caused by polarisation of the electrodes; this does not proceed immediately under the given conditions.

Accuracy

The proposed end-point indication of the chelometric determination of iron(III) permits the determination of 1–150 mg of iron in a volume of 150 ml with reliable accuracy. The results of some titrations are summarised in Table I. The results from this table (with the exception of the results of the titration of 1–2 mg of iron, when the error is greater) give a mean relative error of ±0·8%.

Table I

Fe(III), *mg*		0·05*M* EDTA, *ml*		Difference	
Present	Found	Theory	Found	mg	%
1·03	1·06	0·33	0·34	+0·03	+2·91
2·06	2·09	0·66	0·67	+0·03	+1·46
6·18	6·12	1·98	1·96	−0·06	−0·97
15·41	15·41	5·20	5·20	0·00	0·00
30·83	30·68	10·40	10·35	−0·15	−0·52
51·38	51·53	17·35	17·40	+0·15	+0·29
82·21	81·62	27·70	27·50	−0·59	−0·73
102·76	103·40	34·68	34·90	+0·64	+0·63
154·14	155·53	52·03	52·50	+1·39	+0·90

Selectivity

The selectivity of the proposed titration was verified by the titration of 15·41 mg of iron(III) under defined conditions (pH 1·3–2·5; 20°; 1·0 V) in the presence of a series of foreign ions. The results have shown that even a high concentration of nitrate, sulphate, phosphate, acetate, chloride and borate does not interfere. Also, many metals do not interfere, *e.g.*, cobalt, lead, zinc, cadmium, calcium, barium, strontium, magnesium, manganese, uranium(VI), iron(II) and titanium(IV). On the other hand, even small concentrations of thallium(III) interfere in the titration of iron(III). Indium, gallium, zirconium, thorium and aluminium are titrated together with iron and thus interfere in the determination. Greater amounts than 50 mg of nickel and 80 mg of copper also interfere. Some metals can be masked with fluoride ions, particularly aluminium and also thorium and zirconium,[10] as in the titration of iron(III) with two platinum electrodes.[6]

Analytical application

The described chelometric titration has a similar analytical application to the titration with an indication system of two platinum electrodes.[6] The described procedure is probably best applied to the determination of iron(III) in the presence of iron(II) in various metallurgical materials.[10]

CONCLUSION

The present study has shown the possibility of replacing the two platinum electrodes with two graphite electrodes in the biamperometric titration of iron(III) with

EDTA. The obtained results are of the same accuracy and of the same selectivity. In an unbuffered medium the determination can be carried out at pH 1·1–2·5 and in a buffered medium at pH 1·1–4·2. If a microammeter is used for indicating the end-point, a higher applied potential than 0·6 V should be used.

The graphite electrodes are much cheaper than the platinum ones, which is an advantage in routine analysis. Another advantage is the possibility of determining iron(III) in an acidic medium at room temperature, which was impossible using two platinum electrodes.

Future papers in this series will present the utilisation of amperometry with two identical electrodes for the chelometric determination of some other metals which can be titrated with EDTA, *e.g.*, thorium, indium, gallium, zirconium, copper and rare earths.

As in the case of the titration of iron(III) with EDTA using two platinum indicator electrodes, it is not yet possible to give an exact explanation of the electrode reactions involved in the titration with two carbon electrodes.

In particular, the decrease of current during the titration before the equivalence point cannot yet be explained satisfactorily. An increase of current after the equivalence point was found in the chelometric titration of all metals, provided that indication with two identical electrodes of platinum or of carbon was used and, of course, the pH was kept at the optimum value for each titration. This phenomenon extends the previous presumption that the described biamperometric titrations with EDTA are possible only with metals forming redox systems. Metals which do not form redox systems have a different character in their titration curves. Because the metal ion and also its complex do not give the electrode reaction over a wide potential interval, there are no changes of current before the equivance point. Immediately after the equivalence point the presence of a minimum amount of free EDTA (which takes part in the electrode reaction) causes an increase in the current.

Zusammenfassung—Zur Anzeige der biamperometrischen Titration von Eisen(III) mit EDTA wurden zwei Kohle-(Graphit-) elektroden verwendet. Befriedigende Ergebnisse wurden in einem weiten Bereich der angelegten Spannung erhalten. Die absoluten Stromwerte hängen linear von der angelegten Spannung ab. Bei 0,6 bis 2,0 V gehen die Stromdifferenzen während der Titration von einigen μA bis zum Zehnfachen davon. Der Einfluß von pH, Spannung und Temperatur auf die Titration wurden untersucht sowie der Einfluß von Störelementen. Unter optimalen Bedingungen ist die Bestimmung sehr selektiv und genau. Man kann 1–150 mg Eisen(III) bestimmen.

Rêsumê—Pour l'indication du dosage biampérométrique du fer(III) au moyen d'EDTA, on a utilisé deux électrodes de carbone (graphite). Des résultats satisfaisants ont été obtenus dans un large domaine de potentiels appliqués. Les valeurs absolues du courant sont liées linéairement aux valeurs du potentiel appliqué. A un potentiel de 0,6–2,0 V, les différences de courant durant le dosage vont de plusieurs μA à dix fois ces valeurs. On a étudié les influences du pH, du potentiel appliqué et de la température sur le dosage; on a examiné l'influence des éléments interférents. Dans des conditions optimales, le dosage est hautement sélectif et précis. Il est possible de doser 1–150 mg de Fe(III).

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XVIII*

MASKING OF IRON WITH FLUORIDE

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Summary—Very simple conditions have been found for the quantitative precipitation of iron in an acidic medium as K_3FeF_6. This facilitates the complexometric determination of a number of elements, such as copper, lead, nickel, cobalt, zinc and cadmium, in the presence of iron, aluminium, titanium and the rare earths.

TRIETHANOLAMINE has been used[1,2] to mask iron and aluminium in the determination of manganese, nickel, calcium and magnesium in ores, rocks and minerals, but it screens iron completely only in alkaline solution. It cannot be used if copper or cobalt are to be determined because its complexes with these metals are sufficiently stable to prevent complete reaction with EDTA. Flaschka and Püschel[3] have screened iron(II) with cyanide, but the method is unselective and has not found application in routine work.

The problem of screening iron in an acidic medium has not hitherto been satisfactorily solved. Doornbos, Ab and Faber[4] precipitated iron as potassium hexafluoroferrate(III) and then titrated copper with EDTA using Glycinethymol Blue as indicator,[5] but some of the copper was adsorbed on the precipitate and a double titration was required to overcome this difficulty. The literature contains conflicting statements about the screening and interference effects of fluoride in the determination of iron with EDTA. Accordingly, we examined the masking of iron(III) with ammonium, sodium and potassium fluorides in the presence of nitrate. We found that ammonium fluoride was without effect on the indirect determination of iron by back-titration of an excess of EDTA, whereas sodium and potassium fluorides gave precipitates of the hexafluoroferrate(III) which were sufficiently stable not to react with EDTA. This means that with a mixture of aluminium and iron it is possible to screen aluminium alone with ammonium fluoride or both aluminium and iron with a mixture of potassium and ammonium fluorides. A detailed study has yielded a simple method for the screening of iron, aluminium, titanium and lanthanides, which can be used for the analysis of alloys, *etc.*, containing these elements.

EXPERIMENTAL

Reagents

Solutions of EDTA, DCTA, iron(II), lead(II), aluminium(III), zinc(II), cadmium(II) and copper(II) were made $0{\cdot}05M$ and their concentrations were checked complexometrically. The following solutions were also prepared:— $0{\cdot}1M$ sodium fluoride, $1M$ potassium hydrogen fluoride, $2M$ ammonium fluoride, $1M$ nitric acid, 25% potassium carbonate and 0·2% Xylenol Orange. Solid urotropine and ammonium fluoride were also used.

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* Part XVII: *Talanta*, 1964, **11**, 1613.

Procedure

Add ammonium fluoride to 50–100 ml of the acid solution (0·3–0·5*M* HNO_3) containing up to 60 mg of iron. Cover the vessel containing the solution with a watch-glass and add 25% potassium carbonate solution. Adjust the pH to 5·0–5·5 with solid urotropine, and let the solution stand for 5 minutes with occasional stirring. Add a known volume of EDTA or DCTA, and titrate the solution with 0·05*M* lead nitrate, using Xylenol Orange as indicator. If all the iron has been precipitated, the amounts of EDTA or DCTA taken and found are the same. The results are shown in Table I, from which the optimum concentrations of ammonium fluoride, potassium hydrogen fluoride and potassium carbonate to be added can be deduced.

TABLE I.—PRECIPITATION OF IRON WITH FLUORIDES

Taken	Added		Back-titration		Found
Fe(III), *mg*	F, *ml*	25% K_2CO_3, *ml*	0·05*M* complexan, *ml*	0·05*M* Pb(II), *ml*	Fe(III), *mg*
2·87	10^a	5	3·00 E^c	1·98	2·87
			2·96 D	1·99	2·72
2·87	10^a	10	3·00 E	2·21	2·20
			2·96 D	2·15	2·36
2·87	10^a	20	3·00 E	2·05	2·65
			2·96 D	1·98	2·78
2·87	10^a	30	3·00 E	2·10	2·51
			2·96 D	2·10	2·51
2·87	20^a	5	3·00 E	2·50	1·40
			—	—	—
2·87	20^a	10	3·00 E	2·78	0·61
			2·96 D	2·98	—
2·87	20^a	20	3·00 E	2·98	0·06
			2·96 D	2·99	—
2·87	20^a	30	3·00 E	2·97	0·08
			—	—	—
2·87	20^b	30	3·00 E	3·00	—
			—	—	—
14·34	10^a	10	9·86 D	9·25	1·70
14·34	10^b	20	10·00 E	9·83	0·47
14·34	20^b	10	10·00 E	9·95	0·14
14·34	20^b	20	10·00 E	10·03	—
14·34	20^b	30	10·00 E	9·98	0·06
57·36	10^a	10	25·00 E	7·90	34·88
57·36	10^a	20	25·00 E	26·90	0·28
57·36	20^b	—	24·66 D	27·70	—
57·36	20^b	10	25·00 E	24·93	0·20

[a] 2*M* NH_4F; [b] 1*M* KHF_2; [c] E = EDTA, D = DCTA.

It was found that the iron must be precipitated from a volume not greater than 100 ml, and the amount of precipitant needed was constant, irrespective of the amount of iron present; this meant that larger amounts of iron were more easily precipitated than small ones. Addition of sodium or potassium hydroxide also resulted in precipitation, but potassium carbonate seemed to be the best reagent to use because the carbon dioxide liberated appeared to promote the precipitation. The ammonium salt could not be precipitated. Once the iron had been precipitated, dilution of the solution to as much as 300 ml had no significant effect on the precipitate.

Determination of zinc, lead, cobalt, copper, etc., in presence of iron (aluminium)

Follow the procedure given above: to the acid solution add 2·5 g of ammonium fluoride neutralised with 25 ml of 25% potassium carbonate as described. Determine all elements indirectly by back-titration of excess of DCTA with lead nitrate using Xylenol Orange as the indicator. In Table II some typical results are given.

TABLE II.—DETERMINATION OF SOME ELEMENTS AFTER MASKING OF OF IRON AND ALUMINIUM

Taken, *mg*		0·05*M* complexan, *ml*	Back-titration	Found, *mg*	Difference, *mg*
Fe	Metal ion		0·05*M* $Pb(NO_3)_2$, *ml*	Metal ion	Metal ion
2·87	10·36 Pb(II)	2·96 DCTA	2·00	9·95 Pb(II)	−0·41 Pb(II)
2·87	207·21 Pb(II)	25·00 EDTA	4·98	207·41 Pb(II)	+0·20 Pb(II)
2·87	2·89 Ni(II)	3·00 EDTA	1·99	2·96 Ni(II)	+0·07 Ni(II)
2·87	68·39 Zn(II)	22·00 EDTA	1·13	68·12 Zn(II)	−0·17 Zn(II)
2·87	3·14 Cu(II)	4·93 DCTA	4·05	2·77 Cu(II)	−0·47 Cu(II)
2·87	57·98 Ni(II)	25·00 EDTA	5·25	57·97 Ni(II)	−0·01 Ni(II)
2·87	5·66 Cd(II)	5·00 EDTA	3·98	5·73 Cd(II)	+0·07 Cd(II)
2·87	113·31 Cd(II)	25·00 EDTA	4·83	113·35 Cd(II)	+0·04 Cd(II)
28·68	10·36 Pb(II)	5·00 EDTA	4·01	10·26 Pb(II)	−0·10 Pb(II)
28·68	3·42 Zn(II)	4·93 DCTA	4·00	3·14 Zn(II)	−0·28 Zn(II)
28·68	3·14 Cu(II)	2·96 DCTA	1·99	3·09 Cu(II)	−0·05 Cu(II)
57·36	10·36 (PbII)	3·00 EDTA	1·92	11·18 Pb(II)	+0·82 Pb(II)
57·36	3·14 Cu(II)	3·00 EDTA	1·98	3·24 Cu(II)	+0·10 Cu(II)
2·81	1·40 Al(III)	5·00 EDTA	3·99	2·82 Fe(III)	+0·01 Fe(III)
2·81	27·99 Al(III)^{a}	2·94 DCTA	1·93	2·82 Fe(III)	+0·01 Fe(III)
1·41	34·99 Al(III)^{a}	3·00 EDTA	2·50	1·39 Fe(III)	−0·02 Fe(III)
28·11	3·14 Cu(II)	2·94 DCTA	2·00	2·99 Cu(II)	−0·13 Cu(II)
13·99					
2·81 1·40 Al(III)	103·91 Pb(II)	15·00 EDTA	4·96	104·05 Pb(II)	+0·14 Pb(II)
20·13 Fe(III)^{b} 20·75 Al(III)^{b}	1·00 Ni(II)	25·00 EDTA	3·80	21·20^{b} Fe(III) + Ni(II)	—

[a] Al masked by 1 g of NH_4F before addition of EDTA; in this case the determination of Fe(III) or another element is carried out.

[b] Ml of 0·05*M* solution.

RESULTS AND DISCUSSION

Precipitation of iron with fluoride

The fluoride complexes of iron(III) are less stable than the EDTA or DCTA complexes. Iron can be determined by the addition of an excess of EDTA and back-titration with lead, even in 1*M* ammonium fluoride solution, without difficulty. If sodium or potassium ions are present, however, precipitation of the alkali metal hexafluoroferrate(III) takes place. The addition of sodium fluoride will mask moderate amounts of iron in this way, but the low solubility of sodium fluoride (4% at room temperature) limits the amount of iron that can be screened. Furthermore, the presence of large amounts of fluoride in the solution causes the end-point of the back-titration to be rather indistinct. Potassium fluoride is more suitable as a reagent, giving a white microcrystalline precipitate, but again a large amount must be added. We have found, however, that the fluoride can be introduced by addition of ammonium fluoride, and the potassium added subsequently, either as the fluoride or some other salt. The precipitate gives no reaction with thiocyanate, hexacyanoferrate(III), ammonia, EDTA or DCTA, but on standing with sodium hydroxide it gives a brown precipitate of hydrous iron(III) oxide.

Interference

It has already been pointed out that aluminium, titanium and the rare earths are also masked. Aluminium (or titanium) can be selectively masked with ammonium fluoride alone (neutralise with aqueous ammonia) and the iron determined. These combined procedures have been used for the analysis of various copper alloys.

The masking of iron fails only in the presence of magnanese. We have observed an unexpected phenomenon: manganese is coprecipitated with fluoride. Probably it comes down as a double fluoride iron, which is more reactive than pure hexafluoroferrate(III) and which always gives a positive reaction for iron with thiocyanate, hexacyanoferrate(III) and ammonia. This unfavourable effect of manganese will be studied further.

Zusammenfassung—Sehr einfache Bedingungen zur quantitativen Fällung von Eisen als K_3FeF_6 in saurem Medium wurden gefunden. Das erleichtert die komplexometrische Bestimmung einer Anzahl von Elementen wie Kupfer, Blei, Nickel, Kobalt, Zink und Cadmium in Gegenwart von Eisen, Aluminium, Titan und seltenen Erden durch Zugabe überschüssiger ÄDTA und Rücktitration mit Blei unter Verwendung von Xylenol orange als Indikator.

Résumé—On a trouvé des conditions très simples pour précipiter quantitativement le fer à l'état de K_3FeF_6 en milieu acide. Ceci facilite le dosage complexométrique d'un certain nombre d'éléments tels que le cuivre, plomb, nickel, cobalt, zinc et cadmium, en présence de fer, aluminium,titane, et des terres rares, par addition d'un excès d'EDTA et dosage en retour au moyen de plomb, le Xylénol Orangé servant d'indicateur.

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DETERMINATION OF MINOR AND TRACE ELEMENTS IN NICKEL BY X-RAY SPECTROMETRY

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Summary—The authors have investigated the applicability of X-ray spectrometry to the analysis of nickel for several elements in the ppm range. Results of the investigation are presented and compared with optical spectrographic analysis as regards sensitivity, precision and accuracy, speed and convenience.

INTRODUCTION

X-RAY spectrometry has become almost commonplace for the determination of major and minor constituents of alloys. It has also been used to determine trace amounts of metals in light matrices, such as rocks, slags, petroleum and solutions. However, when trace element concentrations are to be determined in metals, optical emission spectrography is normally used, even though an overlap in ranges of the two methods is recognised.

Little has been published about the determination of trace concentrations in metals by X-ray spectrometry. Michaelis, Alvarez and Kilday[1] investigated detection limits and interferences and developed analytical curves for twenty elements in low-alloy steels. They found that detection limits for most of these elements were below 100 ppm, but those for silver, arsenic and zirconium were 9, 7 and 6 ppm, respectively. Campbell and Thatcher[2] calculated theoretical limits of detectability for several elements in iron. These ranged from 1 to 8·5 ppm for such elements as manganese, copper, chromium and titanium.

X-ray spectrometry offers some advantages, even in this range; a greater amount of sample contributes to the analysis in a shorter time, and compared with optical emission spectroscopy the spectra are simpler with fewer line interferences. The results reported here compare the X-ray method with an already well-established optical emission method for nickel analysis.

EXPERIMENTAL

Apparatus

Quantometer. An Applied Research Laboratories Vacuum X-Ray Quantometer was used in this work. This instrument comprises a multichannel spectrometer, a power supply, a control cabinet for power to the X-ray tube and an electronic read-out console. Fig. 1 shows a schematic diagram of the spectrometer. Mounted around the sample and X-ray tube are nine channels, each with its own crystal and detector. The six fixed channels are: iron, nickel, aluminum, magnesium, scattered radiation at 0·6*A* and copper. Each of these channels is equipped with the optimum arrangement of crystal; air or vacuum path; detector type, size and window; and slit setting for the particular wavelength involved. Three scanning channels together cover the range from 8·27*A* to 0·36*A*; *i.e.*, silicon and elements of higher atomic number. The wavelength ranges of these scanning channels overlap to some extent (Fig. 1), allowing a choice of vacuum or air channel for some elements. A tenth channel, known as the external standard channel, has a small copper disk in a position to be irradiated by the primary beam; the undispersed radiation from this disk is integrated until a preselected voltage is accumulated. Simultaneously, all channels integrate radiation at their particular wavelengths.

The detectors are Multitrons (non-proportional gas-amplification detectors) and Minitrons (flow Geiger detectors); the signal voltage developed by each is stored in a capacitor. At the completion of integration, as signalled by the external standard channel, the capacitors are discharged sequentially at a rapid rate, driving the chart pen to give readings proportional to the fluorescence radiation intensities.

This array is in a research instrument which is used for many tasks. For the work described, only the copper and iron fixed channels and the vacuum scanner covering the 1·07*A* to 3·77*A* range were used.

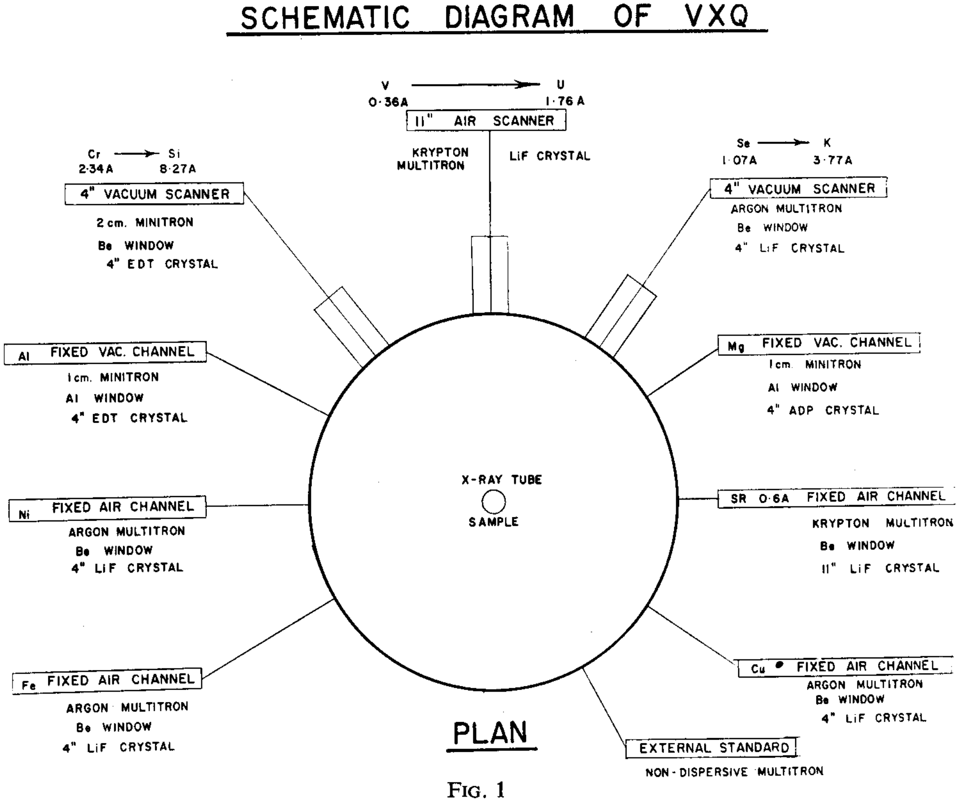

FIG. 1

Mortars and pestles. The mortars and pestles used for this work were fabricated from vacuum-melted nickel ingots. They were originally made for use in the optical emission method, particularly to avoid contamination from magnesium, silicon, aluminium and boron. Although nickel is softer than conventional mortar materials, these mortars have served the purpose very well. They are cleaned by grinding a little high purity nickel powder and the inner surfaces are occasionally polished on a lathe with diamond-impregnated plastic on a cloth backing.

Preparation of samples and standards

Few nickel standards are available commercially. The National Bureau of Standards issues three nickel oxide standards containing several elements in concentrations useful for the X-ray technique,[3] and four secondary standards of Nickel 200 are available from the Huntington Alloy Products Division of the International Nickel Company.[3]

Synthetic standards are useful and can be prepared by adding impurity element solutions to a nickel nitrate solution, evaporating to dryness and reducing the oxides to sponge by heating in hydrogen. Alternatively, oxides, carbonates or other compounds of impurity elements may be added to powdered nickel sponge to make a master standard which can be diluted with pure nickel sponge powder for analytical standards.

Clean samples of millings, drillings, chips, *etc.*, with warm 10% hydrochloric acid to remove surface contamination. Powders or salts are not cleaned. Dissolve 10 g of sample in about 50 ml of

1:1 nitric acid in a platinum dish. Add 20 ml of concentrated nitric acid in 5-ml increments and evaporate the solution slowly on a hot plate at 250°. When the solution has evaporated nearly to dryness, place the dish in a muffle furnace and heat at 400° until the sample has dried and mostly oxidised. Leave the furnace door ajar to allow in air to flush out fumes of nitrogen oxides.

Loosen the sample from the platinum dish, transfer to a porcelain boat and place it in a hinged tube furnace. Pass hydrogen through the tube at about 500 ml/min and raise the temperature to 400°. Maintain this temperature for 20 min to allow complete reduction of the nickel oxide to nickel sponge. Remove the tube assembly from the furnace but maintain the hydrogen flow until the sample has cooled to room temperature. This decreases the danger of pyrophoricity.

Grind the nickel sponge to uniformly fine powder in a mortar.

Prepare briquettes in one of two ways:

(a) Press about 10 g of nickel sponge in a 1⅝″ i.d. mould at about 34,000 psi for 30 sec.

(b) Place about 4 g of boric acid in the mould and tamp with a hardwood plunger to form a flat suface.

Distribute a minimum of 2·5 g of nickel sponge evenly over the boric acid and press at 34,000 psi for 30 secs.

The first method provides a solid nickel disk about 2·5 mm thick. It is the safer method but requires more sample, reagents and time than the other. In the second method, the nickel must be distributed evenly to avoid formation of thin places in the surface, but the smaller amount of sample makes preparation quicker and easier. It is also better when the amount of sample is limited.

Good agreement was found in analyses of the two types of briquette. Density variations might be expected to cause some differences but this was not found critical in the present work. Samples sliced from nickel rods, for example, gave results that agreed reasonably well with those from briquettes.

Thus, one set of curves may be applied to solid or sponge samples. A solid sample must be free from surface contamination and the surface should be ground and polished. The boric acid-backed briquettes are generally used for sponge prepared fromd rillings, chips, powders or irregular samples. Nickel sponge powder, prepared as described here, is composed of irregular particles that bond together well whereas powders composed of spherical particles may crumble when briquetted.

Development of analytical curves

Only the iron and copper fixed channels and one scanning channel were used for this work. General parameters are:

X-ray tube—Tungsten target, end window
Power—50 KV, 35 MA
Collimator—1·25″ diameter
Crystals—Lithium fluoride, 4″ radius of curvature
Detectors—Non-proportional gas-amplification
Mode—Vacuum; sample chamber, X-ray chamber, and scanning channel evacuated.

Air mode can be used for iron and copper at the higher concentration levels, but vacuum is required for titanium and for high sensitivities for other elements.

Calibration curves for different elements and concentration ranges are prepared in the following way. Draw a trial curve on linear co-ordinates with chart readings from zero to one hundred as abscissae and elemental concentrations over the desired range as ordinates. Obtain the desired low and high chart readings from this curve for the low and high standards. Then take actual readings on low and high standards and correlate these mathematically with the desired readings to allow the desired curve to be approximated closely. Make adjustments to attenuators which vary detector sensitivity and to potentiometers which control the zero position and sensitivity of each channel. Analyse all the standards and plot the true curves.

Good straight line curves were obtained for the following elements in nickel (the most suitable concentration ranges given in brackets):—manganese (10–80 ppm, 25–220 ppm and 0·02–0·40%), iron (20–330 ppm, 0·02–0·14% and 0·10–1·20%), cobalt (25–200 ppm, 0·01–0·10% and 0·1–1·0%), chromium (30–350 ppm and 0·02–0·14%), copper (25–500 ppm and 0·01–0·25%) and titanium (30–330 ppm and 0·01–0·10%). The K_α radiation was used except in the case of copper when $K_{\alpha 2}$ radiation was used for the lower concentration range and K_α for the higher. The NiK_α radiation interfered at low concentrations but the $K_{\alpha 2}$ was found to be more sensitive than NiK_β radiation. It is possible to obtain extra zero and sensitivity controls for the channels so that the correct range is automatically available or to provide separate channels for measurement of different ranges, but in the present work, the samples were simply re-analysed under different conditions as required.

Tests were made using ratios of the elements to nickel and to scattered radiation but these appeared to offer no advantage over the use of elemental radiation intensity alone.

Precision

The method used in estimating precision is shown in Table I. Five briquettes were prepared from the same sample and each was analysed five times. Thus, the vertical columns show the reproducibility of sampling and the horizontal columns show the reproducibility of sample orientation and of the instrument itself. In most cases the precision of sampling was as good as instrumental precision.

TABLE I.—PRECISION OF THE DETERMINATION OF MANGANESE IN NICKEL

Run Sample	1	2	3	4	5	$\bar{X}^a$	S^a	V^a
2717-1	39	40	40	41	39	40	0·7	1·8%
-2	42	41	41	41	42	41	0·7	1·7%
-3	41	38	39	41	40	40	1·3	3·3%
-4	42	41	43	42	39	41	1·6	3·9%
-5	42	40	42	43	41	42	1·2	2·9%
$\bar{X}^b$	41	40	41	42	40	41 41		
S^b	1·3	1·2	1·6	1·0	1·3		1·1 1·3	
V^b	3·2%	3·1%	3·9%	2·4%	3·3%			2·7% 3·2%

[a] Instrumental precision
[b] Sampling precision
$\bar{X}$ = Arithmetic mean

$$S = \text{Standard deviation} = \sqrt{\frac{\Sigma(x - \bar{x})^2}{n - 1}}$$

$$V = \text{Coefficient of variation} = \frac{100S}{\bar{X}}$$

All figures but V are in ppm.

DISCUSSION

No attempt was made in this work to define or determine limits of detection. Michaelis *et al.*[1] define detectability as "that concentration at which the coefficient of variation is equal to 100%". Campbell and Thatcher[2] define the minimum detectable amount for the trace concentration range as "that concentration or amount that results in a line intensity above background equal to three times the square root of background for counting times that are not to exceed 10 min."

The maximum coefficient of variation encountered here was 20·9% for iron at 73 ppm. It is believed that the analytical ranges for all of the elements studied can be extended at the lower end with suitable standard samples. However, the limits reached are generally lower than were expected at the outset.

It is not expected that limits of detection by the X-ray method will surpass or even match those that can be obtained by optical emission spectrography for these elements. On the other hand, it may be possible to reach lower detection limits for some refractory elements, such as tantalum or zirconium, by direct X-ray analysis than by direct optical emission analysis.

Precision data for the six elements determined in two samples are presented in Table II. A fairly high order of precision is indicated. A comparison of precision data, made by analysing seventeen pellets of a nickel sample by optical emission analysis and seven briquettes of the same sample by the X-ray method, showed no definite advantage of one method over the other.

TABLE II.—PRECISION OF X-RAY ANALYSIS

Element	Instrumental			Sampling		
	$\bar{X}$	S	V	$\bar{X}$	S	V
			Sample no. 4597			
Manganese	1992	10	0·5%	1996	137	6·9%
Iron	1040	32	3·2	1050	193	18·4
Cobalt	880	13	1·5	880	12	1·3
Copper	330	10	3·0	330	10	3·0
Chromium	107	4·2	4·0	107	8·6	8·0
Titanium	127	7	5·8	127	21	16·0
			Sample no. 1091			
Manganese	136	2·2	1·6%	136	2·6	1·9%
Iron	73	14	20·1	73	16	20·9
Cobalt	75	6	8·4	75	6	8·6
Copper	100	6	5·9	100	6	6·0
Chromium	60	4·9	8·1	60	5·7	9·3
Titanium	75	7·6	10·8	75	7·3	9·8

Average determination, $\bar{X}$, and the standard deviation, S, are given in ppm. Coefficient of variation, V, is in %.

TABLE III.—ACCURACY OF X-RAY ANALYSIS

Element	X-ray	Optical emission	Chemical
	Sample no. 4597		
Manganese	0·199%	0·195%	0·200%
Iron	0·105%	0·115%	0·120%
Cobalt	0·088%	0·090%	0·093%
Copper	0·033%	0·032%	0·030%
Chromium	0·011%	0·012%	0·013%
Titanium	0·013%	0·012%	0·012%
	Sample no. 1091		
Manganese	136 ppm	128 ppm	140 ppm
Iron	73 ppm	82 ppm	74 ppm
Cobalt	75 ppm	67 ppm	64 ppm
Copper	100 ppm	81 ppm	72 ppm
Chromium	60 ppm	59 ppm	67 ppm
Titanium	75 ppm	78 ppm	81 ppm
	Miscellaneous samples		
Manganese	16 ppm	12 ppm	—
Iron	26 ppm	25 ppm	—
Cobalt	59 ppm	59 ppm	64 ppm
Copper	45 ppm	40 ppm	—
Chromium	30 ppm	27 ppm	—
Titanium	26 ppm	22 ppm	—

Accuracy is indicated by comparing X-ray, optical emission and chemical analyses made on the same samples (Table III). Except for copper in sample 1091, where contamination is suspected, agreement is surprisingly good.

It is difficult to compare the speed of the X-ray method with others for the analysis of nickel because of the variety of determinations involved. There are circumstances, however, in which the X-ray method can be most rapid. For example, it allows simultaneous determination of one or more major elements and one or more minor or trace constituents in the same sample when both chemical and spectrographic methods would otherwise be required. The non-destructive nature of X-ray analysis allows re-use of the same sample briquette many times.

Finally, while it is a distinct advantage for those with both types of equipment to be able to check one method against the other, it is perhaps even more important for the X-ray spectrographer to know that the usefulness of his method can be extended to these lower limits.

Zusammenfassung—Die Autoren untersuchten die Anwendbarkeit der Röntgenspektrometrie auf die Analyse mehrerer Elemente in Nickel im ppm-Bereich. Ergebnisse werden vorgelegt und bezüglich Empfindlichkeit, Genauigkeit und Richtigkeit sowie Geschwindigkeit und Bequemlichkeit mit der optischen spektrographischen Analyse verglichen.

Résumé—Les auteurs ont étudié la possibilité d'application de la spectrométrie de rayons X à l'analyse de divers éléments dans le nickel, dans le domaine des parties par million. On présente les résultats de cette étude, et les compare à l'analyse spectrographique optique des points de vue sensibilité, précision et justesse, vitesse et commodité.

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FRONTAL SOLUBILISATION CHROMATOGRAPHY

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Summary—The behaviour of three non-electrolytes has been studied in both frontal and elution chromatography with an ion-exchange resin as stationary phase and an aqueous solution of ethanol as the mobile phase. On the basis of the plate-equilibrium theory, an equation is derived for the breakthrough graph in frontal chromatography. This is simply the integral of the equation for the graph in elution chromatography. Good agreement is found between the experimental breakthrough results and the equation, as well as between the distribution ratios and plate numbers as evaluated by the two chromatographic methods.

INTRODUCTION

ONE of the research projects of this laboratory is the chromatographic resolution of racemic substances with optically-active ion-exchange resins as the stationary phase. Ion-exchange, salting-out[1,2] and solubilisation[2,3] chromatography are included in this project. In preliminary resolutions, frontal chromatography has been more successful than elution chromatography. Because frontal salting-out and solubilisation chromatography had not been studied from either a practical or theoretical point of view, it was desired to perform such an investigation with optically-inactive resins and solutes before attempting further experiments on chromatographic resolutions. In this paper, an equation is derived on the basis of the plate-equilibrium theory for the breakthrough graph in frontal solubilisation chromatography; also, the elution behaviour of three compounds taken singly and in pairs is compared with their frontal behaviour with the aid of the plate-equilibrium theory.

EQUATION FOR FRONTAL SOLUBILISATION CHROMATOGRAPHY

From previously published equations[4] of elution chromatography

$$M = M^* \exp\left[\frac{-p}{2}\left(\frac{C+1}{C}\right)\left(\frac{U-U^*}{U^*}\right)^2\right]$$

$$M^* = \frac{J}{V}\sqrt{\frac{p}{2\pi C(C+1)}}$$

$$V = \frac{U^*}{C+1} \tag{1}$$

it can readily be shown that

$$M = \frac{J}{U^*}\sqrt{\frac{p(C+1)}{2\pi C}}\exp\left[\frac{-p}{2}\left(\frac{C+1}{C}\right)\left(\frac{U-U^*}{U^*}\right)^2\right] \tag{2}$$

where M is the molarity of the migrant solute in any fraction of the eluate;
M^* is the maximum value of M;
U is the volume of eluate collected from the beginning of the addition of the sample;
U^* is U when $M = M^*$;
p is the number of plates in the column;
C is the distribution ratio of the migrant;
V is the interstitial volume of the column;
and J is the quantity (mmol) of sample.

In frontal chromatography

$$J = M_F^* \int_{U=0}^{U=U} dU$$

where M_F^* is the molarity of the solute in the sample solution and hence the ideal final value of M_F, the molarity of the solute in any fraction of the eluate.

If the solute molecules in the first small increment of sample in frontal chromatography are tagged with a radioactive tracer, these molecules would be distributed in the eluate fractions in the same manner as in elution chromatography; the presence or absence of other solute molecules in the portions of liquid subsequently added to the column would not alter the chromatographic behaviour of the tagged molecules. The same statement is true of any subsequent small increment of sample solution, and is also true whether the solute molecules in any increment are tagged or not. Therefore, it follows that the frontal graph is simply the integral of the elution graph. This has previously been found to be true for gas–liquid chromatography.[5–7] Now by writing M_F for M in equation (2) and substituting the value of J from equation (3), we get the equation of the frontal graph

$$M_F = \frac{M_F^*}{U^*}\sqrt{\frac{p(C+1)}{2\pi C}}\int_{U=0}^{U=U} \exp\left[\frac{-p}{2}\left(\frac{C+1}{C}\right)\left(\frac{U-U^*}{U^*}\right)^2\right] dU \qquad (4)$$

In the theory of probability

$$t = \frac{x}{\sigma}.$$

Also from the equations[4]

$$x = U - U^*$$

$$\sigma = U^*\sqrt{\frac{C}{p(C+1)}}$$

it follows that

$$U = U^* + tU^*\sqrt{\frac{C}{p(C+1)}}$$

$$dU = U^*\sqrt{\frac{C}{p(C+1)}}\,dt.$$

Substitution of the last two equations into equation (4) yields

$$Y = \frac{M_F}{M_F^*} = \frac{1}{\sqrt{2\pi}}\int_{U=0}^{U=U} \exp\frac{-t^2}{2}\,dt$$

Values of the integral can be found in probability tables after converting the desired values of U to the corresponding values of t by equation (5). When $U = 0$

$$t \cong -\sqrt{\frac{p(C+1)}{C}} = -\infty.$$

For any reasonable values of p and C, the approximation is valid within the accuracy of the data in probability tables.

It should be noted that the area under the Gaussian graph to be found in probability tables is the area from $t = -\infty$ to $t = t$. Some probability tables give the area from $t = 0$ to $t = t$. These tables can be used by adding 0·5000 to the listed values.

In applying the foregoing equations to the interpretation of a symmetrical experimental breakthrough graph, it should be noted from equation (5) that when $U = U^*$, $t = 0$ and $Y = 0{\cdot}500$. C can then be evaluated by equation (1) after V is determined experimentally or estimated from published data.[8] To determine p, any convenient value of Y is selected, and the corresponding value of U is read from the experimental graph. The value $Y = 0{\cdot}900$ is recommended because the breakthrough curve has a moderate slope at this point, permitting an accurate reading of the corresponding U; then $t = 1{\cdot}282$. By substitution of this value and the appropiate values of U, U^* and C in equation (5), the value of p is calculated. It is desirable to repeat the calculation at $Y = 0{\cdot}100$, $t = -1{\cdot}282$ to test the symmetry of the graph; a symmetrical graph will give identical values of p.

EXPERIMENTAL

A column, 6·25 cm × 3·80 cm², of Dowex 50-X4, 200–400 mesh, was used. The resin had been previously conditioned by successive passages of $1M$ hydrochloric acid, water, 95% ethanol, water, $1M$ sodium hydroxide and water, with several repetitions of the cycle, ending with the resin in the hydrogen form. Finally, a sufficient volume of aqueous ethanol solution (3·00 volumes of 95% ethanol plus 7·00 volumes of water) was passed through the column to equilibrate it. The interstitial volume of the column was 7·85 ml.

Acetophenone, nitrobenzene and β-naphthol of the best available grade were used without further purification. Each of these compounds was subjected to both elution and frontal chromatography with aqueous ethanol of the foregoing composition as eluent or solvent, respectively. In frontal chromatography the concentrations of solutes were between 4×10^{-5} and $3 \times 10^{-4}M$. Eluate fractions of 3·60 ml were collected automatically and analysed by ultraviolet spectrophotometry. Elution or breakthrough graphs were plotted in all cases and used to evaluate C and p for the solute(s) present. A less extensive investigation was also made of the behaviour of β-naphthol in both elution and frontal chromatography with Dowex 50-X8 as the stationary phase.

RESULTS

In most of the breakthrough graphs, the final concentration of the eluate fell a little short of the concentration of the feed solution. This may be the result of the presence in each of the three solutes investigated of a small percentage of a more tenaciously absorbed impurity. If $M_F{}^*$ in equation (6) is taken as the concentration on the plateau after the breakthrough, the experimental curves follow equation (6) very closely. A typical example of the breakthrough graphs of two solutes in one solution is shown in Fig. 1. The maximum difference between the concentration of any fraction of eluate and the value calculated by equation (6) from the values of C and P of experiments 8 and 19 of Table I was only $3 \times 10^{-6}M$.

The elution graphs were nearly perfect Gaussian curves. A comparison of the

TABLE I.—SUMMARY OF CHROMATOGRAPHIC RESULTS

No.	Compound studied	Other compound present	Resin[a]	Type	Flow rate, *cm/min*	*C*	*P*
1	$C_6H_5NO_2$	None	B	elution	0·18	8·06	42
2	$C_6H_5NO_2$	None	B	frontal	0·18	7·82	38
3	$C_6H_5NO_2$	β-$C_{10}H_7OH$	B	elution	0·18	8·04	41
4	$C_6H_5NO_2$	β-$C_{10}H_7OH$	B	frontal	0·18	8·10	38
5	$C_6H_5COCH_3$	None	B	elution	0·18	5·72	31
6	$C_6H_5COCH_3$	None	B	frontal	0·18	5·50	32
7	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	B	elution	0·18	5·68	33
8	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	B	frontal	0·18	5·59	33
9	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	elution	0·18	5·67	24
10	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	elution	0·25	5·32	23
11	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	elution	0·31	5·23	22
12	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	elution	0·46	5·08	18
13	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	frontal	0·46	5·18	19
14	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	elution	0·70	5·08	13
15	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	frontal	0·70	5·28	12
16	β-$C_{10}H_7OH$	None	B	elution	0·18	17·7	33
17	β-$C_{10}H_7OH$	None	B	frontal	0·18	18·3	33
18	β-$C_{10}H_7OH$	$C_6H_5COCH_3$	B	elution	0·18	17·7	31
19	β-$C_{10}H_7OH$	$C_6H_5COCH_3$	B	frontal	0·18	18·3	33
20	β-$C_{10}H_7OH$	$C_6H_5NO_2$	B	elution	0·18	17·4	31
21	β-$C_{10}H_7OH$	$C_6H_5NO_2$	B	frontal	0·18	17·9	33
22	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	elution	0·18	17·9	23
23	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	frontal	0·18	17·6	28
24	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	elution	0·25	16·0	19
25	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	elution	0·31	16·0	17
26	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	frontal	0·31	17·2	15
27	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	elution	0·46	15·3	12
28	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	elution	0·70	15·2	8
29	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	frontal	0·70	16·5	7
30	$C_{10}H_7OH$	None	B	elution	0·46	15·7	18
31	$C_{10}H_7OH$	None	B	frontal	0·46	16·7	16
32	$C_{10}H_7OH$	None	B	elution	0·70	15·3	13
33	$C_{10}H_7OH$	None	B	frontal	0·70	16·8	13

[a] Resins A and B refer to two different columns of Dowex 50-X4.

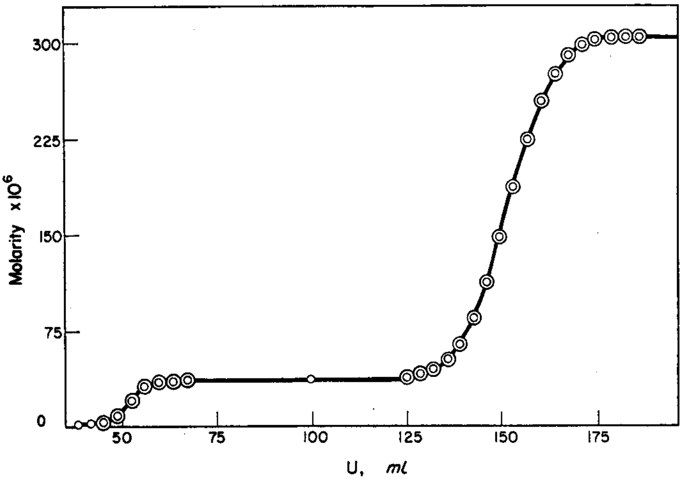

FIG. 1.—Frontal graph of a solution $36{\cdot}2 \times 10^{-6} M$ in acetophenone and $271{\cdot}0 \times 10^{-6}$ M in β-naphthol at 0·18 cm per min (see text for other experimental details). Small circles represent experimental points. Large circles represent points calculated by equation (6).

values of C and P, the number of plates per cm of column height, is given in Table I.

The C values and the P values of experiments 1–4 agree within the experimental error, indicating that these parameters may be evaluated for nitrobenzene by either of the chromatographic techniques with equal reliability. These results also indicate that β-naphthol, which emerges from the column after nitrobenzene, does not affect the chromatographic behaviour of nitrobenzene, in the concentrations used in these experiments.

Experiments 5–8 confirm the same observations in regard to acetophenone in the presence or absence of β-naphthol. Experiments 9–15 show that C and P for acetophenone are slightly influenced by changes in the flow rate. This is an indication of lack of equilibrium.

Experiments 13–33 show slightly larger C values for frontal chromatography than for elution experiments. The differences may be within the experimental error. The presence of acetophenone or nitrobenzene, both of which emerge from the column before β-naphthol, does not affect the behaviour of β-naphthol. Experiments 22–33 indicate again the effect of increasing flow rate.

The experiments, both frontal and elution, with β-naphthol and Dowex 50-X8 yielded P values between 10 and 12 and C values of 12·2.

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Zusammenfassung—Das Verhalten dreier Nichtelektrolyte bei Frontal- und Elutionschromatographie mit einem Ionenaustauscherharz als stationärer und einer wäßrigen Alkohollösung als beweglicher Phase wurde untersucht. Auf Grund der Theorie des Bodengleichgewichts wurde eine Gleichung für den Durchbruchsverlauf bei der Frontalchromatographie abgeleitet. Diese ist einfach das Integral der Gleichung für den Verlauf bei der Elutionschromatographie. Es wurde gute Ubereinstimmung zwischen den experimentellen Durchbruchsdaten und der Gleichung gefunden, ebenso zwischen den Verteilungsverhältnissen und Bodenzahlen, die nach den beiden chromatographischen Methoden gefunden wurden.

Résumé—On a étudié le comportement de trois non-électrolytes en chromatographie frontale et en chromatograhie d'élution, avec une résine échangeuse d'ions comme phase stationnaire et une solution aqueuse d'alcool comme phase mobile. Sur la base de la théorie d'équilibre des plateaux, on a déduit une équation pour le graphique d'"affleurement" en chromatographie frontale. Celle-ci est simplement l'intégrale de l'équation du graphique de la chromatographie d'élution. On a trouvé un bon accord entre les données expérimentales d'"affleurement"et l'équation,et entre les coefficients de distribution et les numéros des plateaux, ainsi qu'ils sont évalués par les deux méthodes chromatograhiques.

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A NEW PRINCIPLE OF ACTIVATION-ANALYSIS SEPARATIONS—IX*

SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF BISMUTH

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Summary—A simple radiochemical separation of bismuth has been developed, based on two dithizone extraction steps, the second of which is a substoichiometric extraction. When copper, gold, mercury, palladium, platinum and silver are not present in interfering amounts, only the substoichiometric dithizone extraction is necessary. The method has been applied to the determination of bismuth by activation analysis in granite and in silicon.

BISMUTH is a mono-isotopic element: on irradiation with thermal neutrons ^{210m}Bi and ^{210}Bi are formed according to following nuclear reactions:

$$^{209}\text{Bi}\ (n, \gamma)\ ^{210m}\text{Bi} \quad \sigma = 0{\cdot}019 \text{ barn, } t/2 = 5{\cdot}0 \text{ day}$$

$$^{209}\text{Bi}\ (n, \gamma)\ ^{210}\text{Bi} \quad \sigma = 0{\cdot}014 \text{ barn, } t/2 = 2{\cdot}1 \times 10^{6} \text{ year.}$$

Of these isotopes only ^{210m}Bi is suitable for activation analysis. Because gamma spectrometry cannot be used for measuring the activity of this beta-emitter (β: 1·15 MeV; $1{\cdot}7 \times 10^{-4}\%$ α), radiobismuth must be isolated in a radiochemically pure state. Of various organic reagents which form extractable chelates with bismuth, such as thenoyltrifluoracetone, thio-oxine, diethylammonium diethyldithiocarbamate and dithizone, the two latter reagents are probably the most suitable for the substoichiometric separation of bismuth. However, in the case of dithizone the quantitative extraction data (log K) of a number of metal dithizonates are well known (Table I).

Reproducibility

Substoichiometric separation is reproducible only when the organic reagent used (dithizone in carbon tetrachloride in the present case) is consumed completely, forming an extractable chelate with the element under investigation. This condition is fulfilled if the pH of the extracted solution corresponds to the value calculated according to the formulae:[2,3]

$$\text{pH} \geqslant -\frac{1}{\text{N}} \log \text{K} - \log 0{\cdot}001\ \text{c}_{\text{HA}} \tag{1}$$

$$\text{pH} \leqslant \text{pK}_{\text{HA}} + \log \text{q}_{\text{HA}} + \log \frac{\text{V}_{\text{org}}}{\text{V}} \tag{2}$$

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For carbon tetrachloride extraction ($V_{CCl_4}:V_{H_2O} = 1:10$), and for the case when 0·1 % of the original concentration of dithizone remains unreacted (0·001 c_{HA}), the pH of the treated solution must lie in the region 2·7 to 8; when 1 % of dithizone remains unreacted, $1{\cdot}7 \leqslant \text{pH} \geqslant 8$ ($K_{HA} = 2{\cdot}8 \times 10^{-5}$; $q_{HA} = 1{\cdot}1 \times 10^{-4}$; $c_{HA} \simeq 10^{-3}$ M). The good agreement of this theory with experimental results can be seen from Figs. 1 and 3.

TABLE I.—EXTRACTION DATA OF METAL DITHIZONATES[1]

Metal	log K[a]	Metal	log K[a]	Metal	log K[a]
Ag^+	7·18	Fm^{3+}	N	Pr^{3+}	N
Al^{3+}	N	Ga^{3+}	1·3	Pu^{3+}	N
				Pu^{4+}	N
Am^{3+}	N	Gd^{3+}	N	PoO_2^{2+}	N
Ba^{2+}	N	Hg^{2+}	26·85	Sc^{3+}	N
Be^{2+}	N	In^{3+}	4·84	Sm^{3+}	N
Bi^{3+}	9·98	La^{3+}	N	Sr^{2+}	N
Bk^{3+}	N	Lu^{3+}	N	Tb^{3+}	N
Ca^{2+}	N	Mg^{2+}	N	Th^{4+}	N
Cd^{2+}	2·14	Mn^{2+}	P	Tl^+	−3·3
Ce^{3+}	N	H_2MoO_4	N	U^{4+}	N
Cf^{3+}	N	Nd^{3+}	N	UO_2^{2+}	N
Co^{2+}	1·53	Np^{3+}	N	Y^{3+}	N
Cu^{2+}	10·53	Ni^{2+}	1·19	Yb^{3+}	N
Dy^{3+}	N	Pb^{2+}	0·44	Zn^{2+}	2·3
Eu^{3+}	N	Pd^{2+}	27	Zr^{4+}	N
Fe^{3+}	N	Pm^{3+}	N		

[a] N = metal not extracted; P = metal partially extracted.

Selectivity

The selectivity of the substoichiometric separation of bismuth with dithizone (H_2Dz) can be evaluated from the data given in Table I. Palladium, mercury, copper and silver (as well as gold and platinum, for which log K values are not known), interfere in the determination, being extracted simultaneously with bismuth even when a substoichiometric amount of dithizone is used. On the other hand, at pH > 9 in the presence of cyanide ions only Bi^{3+}, In^{3+}, Pb^{2+}, Sn^{2+} (log K value not known precisely) and Tl^+ are extracted as dithizonates into carbon tetrachloride.[1] Of these ions, the extraction constant of $In(HDz)_3$ is the closest one to that of $Bi(HDz)_3$, and

$$\frac{[Bi(HDz)_3]\ \text{org}}{[In(HDz)_3]\ \text{org}} = 1{\cdot}4 \times 10^5 \frac{[Bi^{3+}]}{[In^{3+}]}\,.$$

Accordingly, indium will not interfere in the determination of bismuth.[2] From the above it follows that a highly selective radiochemical separation of bismuth, based on the preliminary extraction of bismuth from cyanide solution at pH > 9 using an *excess* of dithizone in carbon tetrachloride, is possible. The bismuth is then stripped from the organic phase with an aqueous solution of mineral acid and substoichiometric extraction of the bismuth carried out with a second portion of dithizone after adjusting the pH to 4 ± 2.

EXPERIMENTAL

Apparatus

Geiger–Müller end-window-counter

pH meter. Radiometer TTT1 (Copenhagen, Denmark).

Spectrophotometer. Zeiss Universal (Jena, DDR).

Separatory funnels. 50- and 150-ml volume.

Reagents

Bismuth carrier. Prepared by dissolving analytical reagent grade metallic bismuth in a small volume of nitric acid, evaporating nearly to dryness, then diluting to an appropriate volume with water (200 μg of bismuth/ml).

Dithizone solution. $7 \times 10^{-4}M$ in carbon tetrachloride.

Acetate buffer (pH 5·6). 0·2*M* acetic acid plus 0·2*M* sodium acetate (1:9).

Borax buffer (pH 10). 0·1*M* sodium hydroxide plus 0·05*M* sodium tetraborate (2:3).

Radiobismuth tracer. The RaE used as a tracer in preliminary experiments was prepared by dithizone extraction from an RaD preparation.

Irradiation

The test samples (*ca.* 0·5–1 g) of granite were sealed in quartz ampoules and irradiated in a neutron flux of $7·5 \times 10^{12}$ neutrons . cm^{-2} . sec^{-1} for 100 hr in a nuclear reactor. The bismuth standard (containing 2 mg of bismuth) was sealed in a quartz ampoule and irradiated simultaneously with the test samples.

Development of Method

Reproducibility

The optimum pH range for substoichiometric separation of bismuth was first investigated. To a series of separatory funnels containing 20 ml of water and 0·5 ml of 10% ascorbic acid, 200 μg of bismuth were added and the pH adjusted (with nitric acid or aqueous ammonia) to different values in the range from 0 to 12. After adding 1·5 ml of dithizone solution (a substoichiometric amount), the extraction was carried out for 3 min and the amount of bismuth present in the organic extract measured either spectrophotometrically at 490 mμ or radiometrically (bismuth carrier labelled with RaE used and the activity of the evaporated organic phase measured by a Geiger–Müller counter). From the curve obtained (Fig. 1) a suitable acidity (pH 2–6) can be seen.

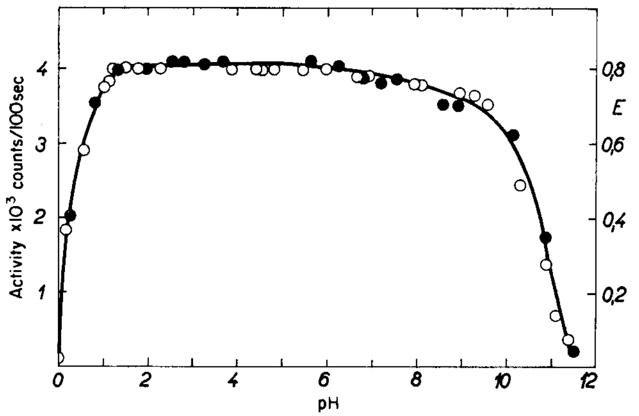

FIG. 1.—Influence of pH on the extraction of bismuth (200 μg) using a substoichiometric amount of dithizone in carbon tetrachloride:

○—spectrophotometric measurements,

●—radiometric measurements.

The time necessary for reaching extraction equilibrium has been tested by extraction of a solution of the following composition: 10 ml of water, 200 μg of bismuth carrier, 5 ml of acetate buffer, 0·5 ml of 10% ascorbic acid; the pH was adjusted to 5 ± 1 with dilute aqueous ammonia. This solution was shaken with 1·5 ml of dithizone solution and the amount of $Bi(HDz)_3$ extracted measured spectrophotometrically; the amount of bismuth extracted was plotted against the time of shaking

(Fig. 2). The extraction was repeated with a second substoichiometric portion of dithizone. An extraction time of 2 min is quite satisfactory.

The reproducibility of the substoichiometric separation was tested in the following way. The acidity of a series of solutions, containing known, increasing amounts of bismuth carrier and 0·5 ml of 10% ascorbic acid, was adjusted to pH 5 ± 1. These solutions were simultaneously extracted with 2·00 ml of dithizone solution for 3 min and the amount of extracted bismuth measured spectrophotometrically (Fig. 3). The same curve has been obtained by means of radiometric measurements using RaE as a tracer.

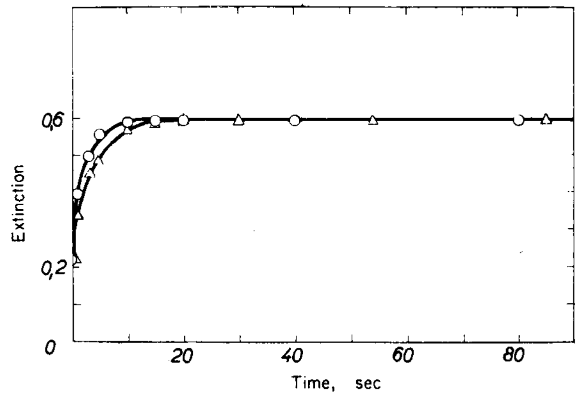

FIG. 2.—Time necessary for reaching extraction equilibrium. Extraction of 200 μg of bismuth with two successive substoichiometric portions of dithizone in carbon tetrachloride at pH *ca.* 4 (spectrophotometric measurements):

○—first extract,
△—second extract.

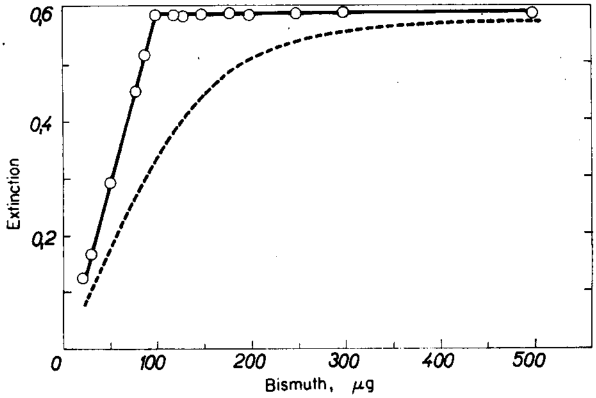

FIG. 3.—Reproducibility of the substoichiometric extraction of bismuth with dithizone at pH *ca.* 4. The dotted line illustrates the influence of a higher acidity (pH < 2).

Selectivity

The selectivity of the substoichiometric separation was investigated by means of microgram amounts of radioisotopes of possible interfering ions. These radioisotopes are mixed with bismuth carrier (400 μg of bismuth) and the proposed radiochemical separation carried out (see ***Procedure***). The selectivity of the separation steps is evaluated from the activities of the organic and aqueous phases, respectively. From Table II it can be seen that only indium, if present in large amounts, interferes in the substoichiometric determination of bismuth by activation analysis. However, this interference is not serious for well known nuclear reasons.

The influence of various anions, which can be present in the extracted solution from dissolution of the test samples or as a component of buffer and masking solutions, has been studied spectrophotometrically. If present in 0·2*M* concentration, the following salts do not interfere in the extraction of $Bi(HDz)_3$ at pH *ca.* 10 (percentage extraction stated in parenthesis): ammonium acetate (95%), sodium tartarate (95%), ammonium citrate (95%), sodium sulphate (95%) ammonium chloride (75%), sodium phosphate (80%), ammonium fluoride (0·1*M* – 60%), ammonium fluoride and boric acid (0·1*M* + 0·01*M*; –95%), potassium cyanide (95%) and sodium tetraborate (95%).

TABLE II.—INTERFERENCE WITH THE EXTRACTION OF BISMUTH CAUSED BY THE ADDITION OF RADIOACTIVE TRACERS[a]

Radioisotope added	^{204}Tl	^{72}Ga	^{114}In	^{110}Ag	^{203}Hg	^{64}Cu
Total activity added,[b] *cpm*	54,560	16,020	15,300	20,220	25,300	18,210
Activity of dithizone extract from cyanide medium, *cpm*	48,720	30	15,120	18	150	60
Activity of HNO_3 strip solution, *cpm*	32,880	0	11,520	0	0	(5)
Activity of substoichiometric extract, *cpm*	0	0	81	0	0	0
%	0	0	0·5	0	0	0

[a] 400 μg of bismuth present as carrier, interferring metals present in microgram amounts.
[b] Only one-tenth of the total activity was actually measured.

Procedure

Dissolve the finely pulverised irradiated sample of granite in a mixture of nitric, hydrofluoric and sulphuric acids in the presence of bismuth carrier (200 μg of bismuth). Evaporate the solution to the appearance of fumes of sulphuric acid (nearly to dryness). Add 20 ml of hot 0·1*M* nitric acid and transfer to a 150-ml separatory funnel, then add 10 ml of 2*M* tartaric acid (to prevent the hydrolysis of aluminium) and 5 ml of 10% ascorbic acid, followed by 6*M* aqueous ammonia dropwise to pH 6–10.

Add 10 ml of 10% potassium cyanide and 5 ml of borax buffer (pH now *ca.* 10). Extract with three successive 5-ml portions of dithizone solution for 2 min. Wash the combined organic extracts with water, transfer to a 50-ml separatory funnel, then strip the bismuth with 5 ml of 2·8*M* nitric acid and 1 ml of 10% ascorbic acid by shaking for 2 min. Add 5 ml of acetate buffer to the separated aqueous phase and adjust the pH to 5 ± 1. Finally, carry out the substoichiometric extraction using 1·5 ml of dithizone solution for 2 min. Evaporate to dryness 1·0 ml of the organic extract on a counting tray on which a disc of filter paper has been placed, and mount for counting.

An appropriate amount of bismuth standard is treated and counted in the same way. The amount of bismuth (y) present in the test sample is calculated from the relationship[3]

$$y = y_s \frac{a}{a_s}$$

where y_s is the amount of bismuth present in the standard sample, and a and a_s are the activities isolated substoichiometrically from the test and standard samples, respectively.

Pure silicon can be treated in a similar way to that described above for samples of granite.

RESULTS AND DISCUSSION

The results of the analysis of granites and pure silicon by the developed procedure are summarised in Table III. The radiochemical purity of the substoichiometric extract was checked by decay measurements (Fig. 4) and by the method of successive substoichiometric extracts. The latter uses two successive, substoichiometric (1·5-ml) portions of extracting agent. In this way two extracts are obtained from the test sample for measuring activities a' and a''. If these activities are equal, it can be judged that not only the reproducibility of the substoichiometric separation (see also Fig. 3) but also the radiochemical purity of the extracts obtained is satisfactory.

Previous radiochemical separations of bismuth developed by different authors[4–8] for the activation analysis of various materials are rather complicated and time consuming. In comparison, the radiochemical procedure now described is simpler, because it is based on two dithizone extraction steps, the second being the substoichiometric one. The selectivity of this method has been demonstrated by its application to the analysis of granite and silicon. When silver, copper, mercury, gold, palladium and platinum are not present in interferring amounts in the test material, the proposed procedure can be further simplified by using only the final substoichiometric dithizone extraction.

TABLE III.—SUBSTOICHIOMETRIC DETERMINATION OF BISMUTH IN GRANITES AND SILICON

Sample	Granite I[a]	Granite II[a]	Granite II[a]	Silicon[c]
Weight, *g*	0·9237	0·5480	0·5482	4·5033
Amount (y_s) of Bi present in standard, *μg*	8·0	8·0	8·0	8·0
Activity obtained from test sample,[b] *a′*	518	263	207	131
a″	534	219	212	—
Activity obtained from standard sample, a_s	456	456	456	5461
Amount of bismuth found, *μg*	9·1	4·6	3·6	0·19
	9·4	3·8	3·7	—
%	1·0 × 10^{-3} [d]	7·7 × 10^{-4} [d]	6·7 × 10^{-4} [d]	4·2 × 10^{-6}

[a] Activities, expressed in c/100 sec, are mean values from 10 measurements corrected for background and decay.

[b] *a′* = first substoichiometric extract; *a″* = second substoichiometric extract.

[c] Activity expressed in c/1000 sec.

[d] Of the order of 10^{-3}% of bismuth was found spectrographically.

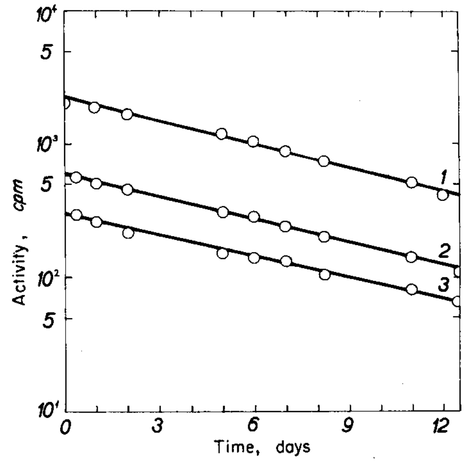

FIG. 4.—The decay curves of dithizonate extracts obtained from irradiated samples of:
1—bismuth standard,
2—granite I,
3—granite II.

Acknowledgement—The authors thank Professor Dr. V. Majer and Dr. M. Williams for their interest in this work and critical discussion.

Zusammenfassung—Eine einfache radiochemische Methode zur Abtrennung von Wismut wurde entwickelt. Sie beruht auf Extraktion mit Dithizon in zwei Stufen; bei der zweiten Stufe wird unterstöchiometrisch extrahiert. Wenn Kupfer, Gold, Quecksilber, Palladium, Platin und Silber nicht in störenden Mengen anwesend sind, ist nur die unterstöchiometrische Extraktion mit Dithizon notwendig. Die Methode wurde auf die aktivierungsanalytische Bestimmung von Wismut in Granit und in Silicium angewandt.

Résumé—On a mis au point une méthode simple de séparation radiochimique du bismuth, basée sur deux stades d'extraction à la dithizone, la seconde étant une extraction substoechiométrique. Celle-ci est seule nécessaire lorsque cuivre, or, mercure, palladium, platine et argent ne sont pas présents en quantités susceptibles d'interférer. On a appliqué la méthode au dosage du bismuth par analyse par activation dans le granit et le silicium.

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DETERMINATION OF COPPER IN SEA WATER BY ATOMIC ABSORPTION SPECTROSCOPY

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Summary—A commerical atomic absorption spectrophotometer is used without modification to establish the most suitable operating conditions for the determination of copper. Using the direct method of spraying aqueous solutions of copper into the flame, the minimum copper which can be determined is about 25 μg/litre. However, this method is not suitable for determining copper in sea water. A method based on the extraction of the copper-ammonium pyrrolidine dithiocarbamate complex into ethyl acetate and spraying of the organic extract into the flame is satisfactory, and it gives a marked increase in sensitivity.

INTRODUCTION

THE determination of trace metals has in recent times gained considerable analytical significance. Many methods and techniques have been applied to this end with varying degrees of success. The development of atomic absorption spectroscopy by Walsh,[1,2] however, provided a technique which has been particularly useful in the determination of trace metals because of its reduced susceptibility to interference. In this respect it is superior to emission spectroscopy and flame photometry, two techniques of great value in trace metal determination.

In the short time since its innovation, a large volume of literature has appeared on the application of this technique to the determination of small amounts of metals in various materials.[3] Allan[4] used the technique successfully for the determination to trace metals in agricultural materials, while Menzies[5] reported on its use for the analysis of industrial alloys and Erinc and Magee[6] used it for the determination of palladium in platinum metal alloys.

Sea water contains very small concentrations of metals such as copper, zinc and nickel. Fabricand *et al.*[7] employed atomic absorption spectroscopy for the determination of metal concentrations in water from the Pacific and Atlantic Oceans. However, investigations of this type are not numerous and the lack of reliable measurements on trace constituents has been pointed out by several authors.[8] The present work was undertaken to investigate the minimum amount of copper which could be determined by atomic absorption spectroscopy, with the purpose of using the method for the determination of copper in sea water.

EXPERIMENTAL

Apparatus

A standard Uvispek H 700 spectrophotometer, fitted with a Hilger H 1100 atomic absorption attachment, was used. For the line source a standard Hilger and Watts copper hollow-cathode lamp was employed. Although trends in the results indicated that modification of the spraying chamber might be an advantage, no alterations were made to the standard commercial equipment.

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The regular arrangement of equipment and method of operation were used throughout. These have been described often, elsewhere, and will not be repeated here. Gatehouse and Willis[9] established conditions for the determination of copper by the atomic absorption method. However, the instrument used was different to that in the present work and experience has shown that conditions are very much dependent on the apparatus used. The optimum conditions for the particular instrument used n the present work were, therefore, investigated.

RESULTS AND DISCUSSION

Effect of lamp current

In their work Gatehouse and Willis[9] found that the spectral line at 3248 Å was the most sensitive for measurement of the absorption of copper. In investigations on the lamp current, therefore, this wavelength was used. An aqueous solution of copper sulphate ($CuSO_4 \cdot 5H_2O$), containing 100 μg atom of copper/litre,* was sprayed into the flame. The results are shown in Table I. Maximum response was obtained at a lamp current of 4·5 mA, which was, therefore, used in subsequent investigations.

TABLE I.—EFFECT OF LAMP CURRENT

Lamp current, *mA*	Response (optical density)
4·5	0·112
10·0	0·105
14·5	0·102
19·5	0·095
24·0	0·094
28·5	0·092
34·0	0·085

(Slit width: 0·25 mm; air pressure: 20 lb/in.^{2}; propane gas pressure: 2 lb/in.^{2})

Effect of slit-width

In the instrument used by the earlier workers,[9] a slit-width of 3 mm was considered best for maximum absorption by copper at 3248 Å. The spectrophotometer used in the present work, however, provided for slit-widths up to a maximum of 2 mm. It was necessary, therefore, to determine the optimum slit-width. The results (average values for a number of readings) are shown in Table II. Although the response

TABLE II.—EFFECT OF SLIT-WIDTH

Slit width, *mm*	Response (optical density)
0·50	0·108
0·45	0·108
0·40	0·110
0·35	0·110
0·30	0·110
0·25	0·111
0·20	0·111
0·15	0·111
0·10	0·120

(Wavelength: 3248 Å; lamp current: 4·5 mA; air pressure: 20 lb/in.^{2}; propane gas pressure: 2 lb/in.^{2}; solution sprayed: 100 μg of copper atom/litre.)

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* μg atom/litre = μg × atomic weight/litre

increases at lower slit-widths, it was not considered desirable to use these because results below a slit-width of 0·25 mm were not easily reproducible. For a lamp current of 4·5 mA, the best results were always obtained using a slit-width of 0·25–0·30 mm.

Effect of air/propane gas pressures

An air/propane gas flame was used throughout the work. Investigation of the gas pressure was considered necessary because, according to Elwell and Gidley,[3] the time for a droplet to pass through 1 cm of flame is about 10 msec, so that lowering the gas pressure should decrease the velocity of the gases and, consequently, the velocity at which the droplets pass through the flame, thereby enhancing the sensitivity. The results for air and propane gas pressures are shown in Tables III and IV, respectively.

TABLE III.—EFFECT OF AIR PRESSURE

Air pressure *lb/in.*^{2}	Response (optical density)
20	0·124
22	0·125
24	0·132
25	0·134
27	0·137
29	0·138
30	0·137
32	0·134
34	0·132

(Slit-width: 0·25 mm; lamp current: 4·5 mA; propane gas pressure: 2 lb/in.^{2}; wavelength: 3248 Å; solution sprayed: 100 μg atom of copper/litre.)

TABLE IV.—EFFECT OF PROPANE GAS PRESSURE

Propane gas pressure, *lb/in.*^{2}	Response (optical density)
1	0·126
1·5	0·129
2	0·134
2·5	0·134
3	0·133

(Slit-width: 0·25 mm; air pressure: 29 lb/in.^{2}; lamp current: 4·5 mA; wavelength: 3248 Å; solution sprayed: 100 μg atom of copper/litre.)

Increase in the propane gas pressure above 3 lb/in.^{2} produced a tendency to luminosity in the flame. From the point of view of response and reproducibility an air pressure of 29 lb/in.^{2} and a propane gas pressure of 2 lb/in.^{2} were found to be the most suitable for aqueous solutions of copper.

Effect of absorbance path

In spraying aqueous solutions of copper, the height of the *absorbance path** in the flame relative to the base of the flame was found to have a marked influence on

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* This is more fundamental than the *burner position.*

the response (Table V). It will be seen that an aqueous solution of copper sprayed into the flame gives maximum response at high absorbance path.

TABLE V.—EFFECT OF ABSORBANCE PATH

Absorbance path	Response (optical density)
Low	0·040
Low medium	0·046
High medium	0·052
High	0·053

(Slit-width: 0·25 mm; air pressure: 29 lb/in.^{2}; lamp current: 4·5 mA; wavelength: 3248 Å; solution sprayed: 40 μg atom of copper/litre).

Analytical results

Using the above optimum conditions for maximum response, a series of copper solutions, prepared from copper sulphate, was sprayed into the flame and the response recorded (Table VI).

TABLE VI.—RESPONSE FOR VARYING AMOUNTS OF COPPER

Copper present, *µg/litre*	Response (optical density)
250	0·006
200	0·005
150	0·004
100	0·003
50	0·002
25	0·002
10	—

The values shown for the response are an average of a number of readings at each concentration. Below 50 µg of copper/litre the sensitivity decreases and below 25 µg/litre a sensible response was not obtained.

For different amounts of copper a calibration curve was obtained and is shown in Fig. 1 (curve A).

Copper in sea water

The method was applied to the determination of copper in sea water drawn from the Belfast Lough. Satisfactory results could not be obtained, however, because of interference from other elements present in the sea water, principally sodium. In order to overcome this difficulty with the direct method, a new approach was made by way of copper complexes and their selective extraction into organic solvents.

Behaviour of copper complexes

The use of metal complexes sprayed into the flame from organic solvents is not extensive in atomic absorption spectroscopy. Erinc and Magee[6] determined palladium by extracting the palladium pyridine thiocyanate complex in hexone and spraying the organic extract into the flame. More particularly, Allan[10] formed the ammonium pyrrolidine dithiocarbamate complex of copper and extracted it into ethyl acetate. This extract, sprayed into the flame, gave an enhancement in sensitivity for the copper absorption.

In the present work, the reagent ammonium pyrrolidine dithiocarbamate could not be readily obtained, so that preliminary investigations were begun with the widely used complexing agent for copper, sodium diethyldithiocarbamate. With copper this reagent forms complexes which are readily soluble in carbon tetrachloride, chloroform and xylene. However, all the extracts of the copper complex were found to be unsuitable. Spraying into the flame resulted in an unstable, sooty flame giving inconsistent responses. Further, in the case of carbon tetrachloride, a large volume of chlorine was evolved in the flame. The reagent used by Allan, ammonium pyrrolidine dithiocarbamate was prepared after the method of Malissa and Schoffman.[11] Results using this reagent showed that the copper complex in the ethyl acetate, when sprayed into the flame, yielded an increase 4–6 times that for the same concentration sprayed from aqueous solution. A procedure which was found to operate satisfactorily is as follows.

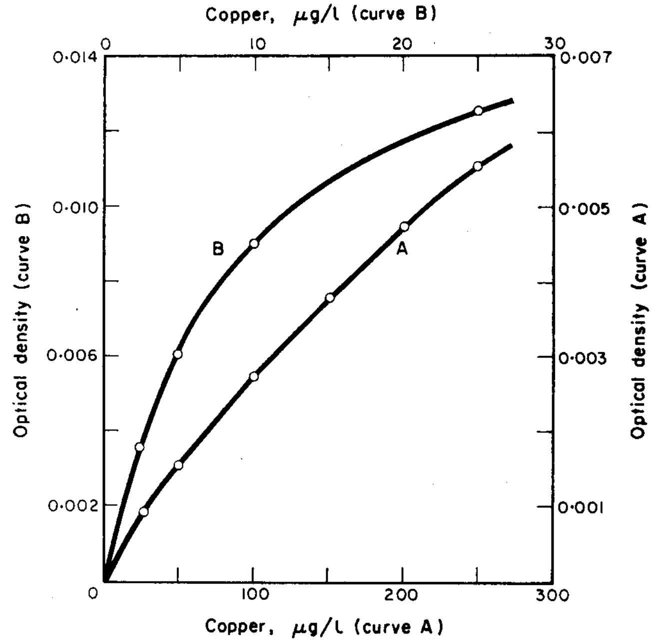

FIG. 1.—Calibration curve for copper:
A—Up to 250 μg of copper/litre (without extraction procedure),
B—Up to 25 μg of copper/litre (with extraction procedure).

Procedure

To 25 ml of an aqueous solution of copper in a 50-ml separating funnel, add 1 ml of 1 % ammonium pyrrolidine dithiocarbamate solution. Shake the mixture well for 15–20 sec, then add 10 ml of ethyl acetate. Shake again for 1 min. After separation of the phases, remove the lower aqueous phase. Filter the acetate phase into a 10-ml volumetric flask and make up to the mark. Employing the conditions derived above for operation of the atomic absorption spectrophotometer (*Note*), spray the acetate extract into the flame and record the response.

Note. Investigations showed that all the conditions determined for aqueous solutions of copper gave optimum response with the acetate extract except for the absorbance path. Results for a 40 μg atom/litre solution of copper extracted into ethyl acetate as the complex are shown in Table VII.

TABLE VII

Absorbance path	Response (optical density)
Low	0·215
Low medium	0·200
High medium	0·130
High	0·110

It will be seen that, unlike the aqueous solution, maximum response occurs at low absorbance path.

Analytical results

Using this procedure the response for copper concentration in the range 2·5 to 250 μg/litre was measured. Results are shown in Table VIII. The results shown at each concentration represents an average value of a number of readings. A calibration curve was prepared for the range of concentrations and is shown in Fig. 1 (curve B).

TABLE VIII.—RESPONSE FOR VARYING AMOUNTS OF COPPER USING EXTRACTION PROCEDURE

Copper present, *μg/litre*	Response (optical density)
2·5	0·011
5	0·014
10	0·017
25	0·021
50	0·026
100	0·033
250	0·051
Blank (Background reading)	0·008

Determination of copper in sea water

It was indicated above that difficulties arise in the direct determination of copper in sea water because of the interference from other elements, particularly sodium.

Before applying the extraction method to the determination of copper in sea water, the influence of large excesses of sodium and magnesium on the method was investigated. To copper solutions of known concentration (2·5–250 μg/litre), sufficient sodium chloride and magnesium chloride were added to make the solutions 16% in the former and 1% in the latter. The solution was then complexed, extracted in the recommended manner and sprayed into the flame. Results are shown in Table IX. Figures in parenthesis are those obtained for solutions of the same concentration of copper, but without the addition of sodium and magnesium chlorides. The result shown at each concentration represents the average of a number of readings

In the presence of sodium and magnesium only, a very small increase in the response was observed. It was supposed that the small increase in the response was

TABLE IX.—EFFECT OF SODIUM AND MAGNESIUM CHLORIDE ON RESULTS FOR COPPER

Copper concentration, *μg/litre*	Response (optical density)
2·5	0·012 (0·011)
5	0·014 (0·014)
10	0·017 (0·017)
25	0·021 (0·021)
50	0·026 (0·026)
100	0·033 (0·033)
250	0·051 (0·051)

from the presence of traces of heavy metal impurities complexed and extracted in the same way as copper. Ethylenediaminetetra-acetic acid (EDTA) was added as a masking agent to the test solution in Table IX before formation of the copper complex and the determinations repeated. In this way the small increase in the response was eliminated. For the determination of copper in sea water the procedure just discussed was used, with the addition of EDTA to the samples before complexing and spraying into the flame.

The sea water was drawn from the Belfast Lough at a depth of 2 ft below the surface and, after sampling, was analysed with the following results:

(a) 2·00 μg/litre.
(b) 1·75 μg/litre,
(c) 1·75 μg/litre,
(d) 2·00 μg/litre,
(e) 1·75 μg/litre.

The average value for these 5 samples is 1·85 μg of copper/litre.

The values obtained are very similar to those obtained by Fabricand *et al.*[7] for sea water drawn from the Altantic and Pacific Oceans and to those of Chow and Thompson.[12] The latter workers used a spectrophotometric method for the determination, while the former employed atomic absorption spectroscopy. It would appear, therefore, that the copper content of the water in the Irish Sea does not vary markedly from that of the Pacific Ocean.

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Zusammenfassung—Ein handelsübliches Spektralphotometer für atomare Absorptionsmessungen ohne Änderungen wird zur Ermittlung der geeignetsten Arbeitsbedingungen zur Kupferbestimmung verwendet. Mit der direkten Methode, bei der wäßrige Kupferlösungen in die Flamme gesprüht werden, ist die Nachweisgrenze für Kupfer etwa 25 μg/Liter. Diese Methode ist aber nicht zur Bestimmung von Kupfer in Meerwasser geeignet. Dieses Problem wird zufriedenstellend gelöst durch Extraktion des Kupfer-Ammoniumpyrrolidindithiocarbamat-Komplexes in Äthylacetat und Versprühen des organischen Extraktes in der Flamme. Mit dieser Arbeitsweise erzielt man eine bemerkenswerte Steigerung der Empfindlichkeit.

Résumé—Afin d'établir le meilleur mode opératoire pour le dosage du cuivre, on a employé sans modification un spectrophotomètre d'absorption atomique commercial. En utilisant la méthode directe de pulvérisation de solutions aqueuses de cuivre dans la flamme, la quantité minimale de cuivre dosable est d'environ 25 μg/litre. Toutefois, cette méthode ne convient pas au dosage du cuivre dans l'eau de mer. Une méthode, basée sur l'extraction du complexe cuivre-pyrrolidine dithiocarbamate d'ammonium en acétate d'éthyle, et pulvérisation dans la flamme de l'extrait organique, est satisfaisante, et offre un accroissement notable de la sensibilité.

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SHORT COMMUNICATIONS

A modification of Leithe's method for determining nitrate

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In the Leithe method,[1] nitrate is reduced with a known amount of iron(II) solution (55 g of $FeSO_4 \cdot 7H_2O$, 20 g of NaCl and 900 ml of 1:1 H_2SO_4/litre) and the excess iron(II) is then back-titrated using ferroïn as indicator.

Although freshly-prepared Leithe reagent gives excellent results, we have found that within 1–2 hr a precipitate appears in the solution, and the blank values begin to decrease in an erratic manner. This experience contrasts with that of Leithe who prepared solutions stable for 1 day or longer.

A reagent stable for at least 5 or 6 days can be simply prepared by dissolving the appropriate amount of $FeSO_4 \cdot 7H_2O$ in 1 litre of water containing HCl; the NaCl and H_2SO_4 necessary to effect the reduction are added separately. Because the reduction depends upon reaction conditions, it has been necessary to determine conditions under which this reagent would give the most satisfactory results.

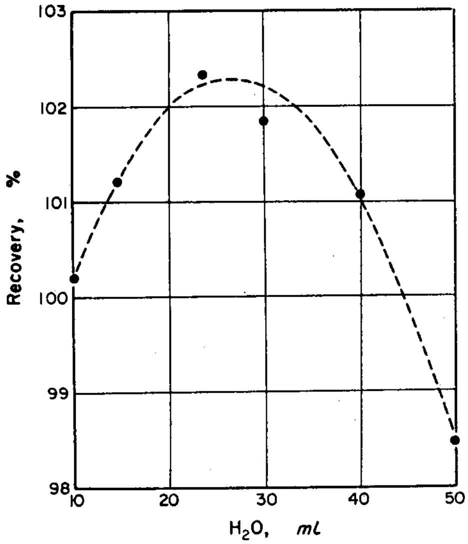
EXPERIMENTAL

Reagents and solutions

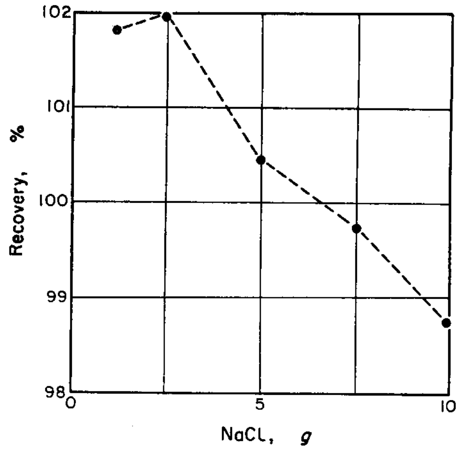
Reagent-grade chemicals were used throughout.

Standard solutions of nitrate were prepared by weighing out the desired amount of either KNO_3 or $NaNO_3$ and diluting to volume.

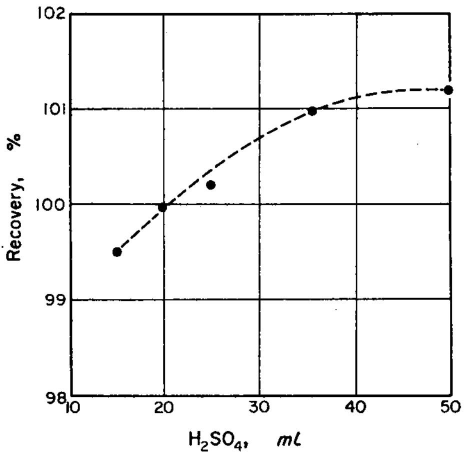
The $FeSO_4$-HCl solution was prepared by dissolving 92 g of $FeSO_4 \cdot 7H_2O$ in 200 ml of water, containing 20 ml of concentrated HCl, and diluting to 1 litre.



a—Effect of H_2O: 5 g of NaCl, 25 ml of H_2SO_4, 40 mg of $NaNO_3$ present.



b—Effect of NaCl: 25 ml of H_2SO_4, 20 ml of H_2O, 40 mg of $NaNO_3$ present.



c—Effect of H_2SO_4: 5 g of NaCl, 20 ml of H_2O, 40 mg of $NaNO_3$ present.

FIG. 1.—The effect of reaction conditions on the determination of nitrate using $FeSO_4$-HCl.

Procedure

The details of the Leithe procedure both for solutions of nitrate and for mixtures of nitrate and nitrite have been described in detail elsewhere.[1] They were followed exactly.

To study the conditions in which the $FeSO_4$-HCl reagent would be a satisfactory substitute for the Leithe reagent, a 10-ml aliquot of $NaNO_3$ solution (4·00 g/litre) was placed in a 250-ml Erlenmeyer flask. A known volume of H_2O, a known weight of NaCl, a 15-ml aliquot of the $FeSO_4$-HCl reagent and a known volume of H_2SO_4 were added in that order. The resulting solution was boiled for 3 min and cooled; 100 ml of H_2O were added and the excess iron(II) titrated with standard dichromate to the ferroïn end-point.

On the basis of the results obtained from the above experiments, known amounts of nitrate were titrated in the following manner: the sample was dissolved in 20 ml of H_2O, and 5 g of NaCl, a 15-ml aliquot of the reagent and 20 ml of concentrated H_2SO_4 were added; from this point on, the sample solutions were treated as previously described. To determine nitrate in mixtures of nitrate and nitrite, only one additional modification was necessary to remove the nitrite interference. After the sample was dissolved in water, 2 g of urea were added; 0·5 ml of concentrated H_2SO_4 was added drop-wise and with vigorous shaking; the nitrate was then determined as before.

RESULTS AND DISCUSSION

The results in Fig. 1(a, b, c) show the effect of reaction conditions on the reduction of the nitrate to $FeNOSO_4$ using the $FeSO_4$-HCl reagent. The effect of chloride on this reagent is similar to the chloride effect on the Leithe reagent.[2] That the amount of water and acid affect the recoveries should come as no surprise, considering the rigorous conditions necessary in the Leithe procedure. Increasing the amounts of NaCl and H_2SO_4 improves the sharpness of the end-point; increasing the amount of water initially present decreases the sharpness of the end-point, and after 50 ml have been added the end-point colour-change is from orange to yellowish-brown, not from orange to *aqua*.

Table I shows the results obtained using this procedure. Urea, recommended by Leithe for removal of nitrite, is effective; but, as the table shows, its effect is limited to about the equivalent of 46 mg of $NaNO_2$. We have not found it necessary to add unglazed porcelain when using our procedure, although Leithe recommends it for his.

TABLE I.—DETERMINATION OF NITRATE

$NaNO_2$, *mg*	$NaNO_3$, *mg*	
	Added	Found
0·00	20·0[b]	20·2
	39·7	39·7 ($n = 4, s = 0·3$)[d]
	40·0[b]	39·9
	59·7[a]	60·1 ($n = 3, s = 0·7$)
	60·0[b]	59·9
	79·6[a]	80·4 ($n = 4, s = 0·8$)
	80·0[b]	80·6
18·1	39·7[a]	39·8 ($n = 3, s = 0·3$)
30·2	39·7[a]	39·5 ($n = 3, s = 0·2$)
40·4	40·0[b]	39·8
46·0	46·8[b]	46·9
60·0	30·8[b]	31·8
		29·6[c]

[a] Two different analysts analysed the same standard.
[b] A second standard analysed by a third analyst.
[c] 4 g of urea used instead of 2.
[d] *n* represents the number of determinations, *s* the standard derivation.

An X-ray diffraction pattern of the precipitate which formed in the Leithe reagent showed it to be $FeSO_4{\cdot}H_2O$ (szomolnokite). If the reagent was prepared in the manner described by Leithe, *i.e.*, by dissolution of the $FeSO_4{\cdot}7H_2O$ and NaCl in 100 ml of H_2O followed by the addition of sufficient cold 50% H_2SO_4 to give 1 litre of solution, precipitation was gradual and, as noted above, did not begin for an hour or so. If the $FeSO_4{\cdot}7H_2O$ and NaCl were dissolved in 550 ml of H_2O and 450 ml of concentrated H_2SO_4 were added, a copious precipitate of $FeSO_4{\cdot}H_2O$ formed immediately; cooling the reaction mixture effected no apparent reduction in the amount of precipitate.

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Summary—A more stable reagent, $FeSO_4$-HCl, can be effectively substituted for the $FeSO_4$-NaCl-H_2SO_4 reagent originally proposed by Leithe for the determination of nitrate. The NaCl and H_2SO_4 necessary to effect a quantitative reaction are added separately to the sample and blanks, rather than being incorporated in the reagent.

Zusammenfassung—Das ursprünglich von Leithe zur Nitratbestimmung vorgeschlagene $FeSO_4$-NaCl-H_2SO_4-Reagens kann mit Erfolg durch eine stabilere Lösung von $FeSO_4$ in HCl ersetzt werden.

Résumé—Le réactif $FeSO_4$-NaCl-H_2SO_4, proposé à l'origine par Leithe pour le dosage des nitrates, peut être efficacement remplacé par un réactif plus stable, $FeSO_4$ en HCl.

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Applications de la chelatometrie—XVI:[*] Emploi du complexe cuivrique de l'E.D.T.A. pour le dosage volumetrique du glucose

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L'EMPLOI des réactifs cuivriques est très répandu pour le dosage des sucres réducteurs; récemment, plusieurs méthodes chélatométriques ont été suggérées pour le dosage du cuivre contenu, soit dans un excès de réactif après réaction, soit dans le précipité d'oxyde cuivreux.

Street[1] est, à notre connaissance, le premier à avoir employé l'E.D.T.A. pour doser le cuivre II dans un réactif utilise en excès; le réactif était de formule classique stabilisé à l'acide tartrique; Knight et Allen[2] puis Roche,[3] reprennent successivement la même technique; le dosage est pratiqué sans filtration en utilisant la murexide comme indicateur. Jäschke[4] filtre le milieu réactionnel pour pouvoir conduire le dosage en tampon ammoniacal sans être gêné par le cuivre I "soluble" dans ces conditions et facilement réoxydé par l'oxygène atmosphérique. Ce procédé est voisin de celui que nous avons indiqué précédemment[5] mais nous opérions alors en milieu tampon pyridiné avec le violet de pyrocatéchine comme indicateur.

En 1954, Bultasova et Horakova,[6] ont décrit une technique dans laquelle l'oxyde cuivreux, isolé, était repris par l'acide nitrique pour permettre son dosage volumétrique par l'E.D.T.A.; une méthode semblable a été mise en oeuvre récemment par Tamura et Miyazaki;[7] ces auteurs utilisent également un réactif cuivrique classique à l'acide tartrique.

En 1953, cependant, l'étude des conditions de réduction par les sucres du complexe cuivrique de l'E.D.T.A. avait été faite par Reiner et Preiss,[8] d'une part, et par Wagreich et Harrow,[9] d'autre part. En 1957, Doss[10] utilisait ce réactif, alcalinisé par la soude, pour réaliser des dosages directs, l'indication du point final étant donnée par le Bleu de Méthylène.

En 1954, Potterat et Eschmann[11] exposent une technique utilisant ce même complexe cuivrique, avec redissolution de l'oxyde cuivreux dans l'acide nitrique suivie d'une mesure volumétrique au moyen de l'E.D.T.A.; diverses applications sont décrites ensuite par ces mêmes auteurs[12–15] puis par Raymond,[16] par Malkus et Fara[18] et par Rentschler *et al.*[19] Hadorn et Biefer[20] étudient l'influence des acides aminés; Hadorn et Suter[21] examinent celle des dextrines et Kupferschmid[22] celle des peptides, peptones et protéines. Malkus[23] suggère une variante dans laquelle la murexide est remplacée par le Bleu de Glycine-Thymol. Hadorn[24] compare la technique originale à celle de la "double polarisation" et à la méthode de Luff-Schoorl;[25–27] après les avoir fait essayer toutes trois par 18 laboratoires sur 8 échantillons de chocolat, il conclut qu'elle est la plus fidèle des trois.

Potterat et Eschmann[11] n'avaient pas manqué de remarquer qu'à chaque atome de cuivre précipité à l'état d'oxyde cuivreux correspondait une molécule d'E.D.T.A. libérée et donc dosable au moyen d'une solution titrée de sulfate de cuivre.

Toutefois, ces auteurs s'étaient heurtés à plusieurs difficultés et avaient définitivement abandonné cette voie. Les difficultés étaient dûes à la présence d'impuretés métalliques, une couleur trop prononcée de la solution et un mauvais virage.

Etant donné l'intérêt présenté par un dosage évitant la séparation et la reprise du précipité, nous avons voulu essayer si, au moins dans le cas d'un sucre "propre", cette voie ne pouvait pas être exploitée. Après précipitation, la mesure de la quantité d'E.D.T.A. libéré a d'abord été tentée au moyen d'un sel de zinc ou de manganèse en milieu tamponné par le chlorure d'ammonium et en présence de Zincon ou de Noir Eriochrome suivant Kinnunen et Merikanto[28] ou Kinnunen et Wennerstrand,[29] mais l'incertitude du virage avec ces sels nous a fait revenir finalement au sulfate de cuivre.

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[*] Article précédent: *Talanta*, 1962, **9**, 97.

D'autre part, nous avons vite renoncé à l'addition de chlorure d'ammonium dont la présence améliorait le virage, mais occasionnait en "dissolvant" l'oxyde cuivreux une réoxydation très rapide de celui-ci même en opérant sous une couche de paraffine comme le conseille Peska.[30] Comme indicateur, nous avons retenu la murexide qui a donné satisfaction à la plupart des auteurs et évite de modifier le pH de la solution après réaction. Nous avons toutefois, observé que, si la concentration de 1 à 2 mmoles par litre indiquée par Schwarzenbach et Flaschka,[17] et rappelée par Potterat et Eschmann,[11] pouvait être portée à une concentration cinq à dix fois plus forte en milieu ammoniacal, elle devait, par contre, être considérée comme un maximum dans le milieu sodique dans lequel nous devions travailler. Une dilution importante s'avérant nécessaire, nous avons résolu le problème en effectuant la réduction dans une fiole jaugée de 100 ml qu'il suffit de compléter ensuite avec de l'eau distillée; un prélèvement de 20 ml additionné d'eau avant titrage nous a permis de satisfaire les conditions de dilution et d'obtenir un virage tout à fait net; cette manière de faire présente, en outre, l'avantage d'éliminer la presque totalité de l'oxyde cuivreux, cette élimination ajoutant encore à la qualité du virage.

PARTIE EXPERIMENTALE

Réactifs utilisés

Réactif cuivrique 0,1 M: nous avons utilisé le réactif décrit par Eschmann[14] mais, en raison de la méthode mise en oeuvre, nous avons dû adopter un procédé de préparation permettant d'écarter tout risque de présence d'E.D.T.A. ou sulfate cuivrique en exces dans la solution. Une fiole jaugée à deux graduations est nécessaire pour cette préparation: celle-ci peut être effectuée dans une fiole de capacité correspondant à l'importance de la consommation de réactif mais nous nous sommes limités à une fiole de 200/220 ml qui offrait l'avantage d'être disponible dans le commerce; pour des capacités plus grandes, la fiole pourrait être obtenue en modifiant le col d'une fiole à simple jauge. 8,4 g d'éthylène-diaminotétracétate disodique bien sec sont dissous avec 64,5 g de carbonate de sodium décahydraté dans le minimum d'eau distillée nécessaire; 5,4 g de sulfate cuivrique pentahydraté, préalablement dissous dans un peu d'eau distillée, sont ajoutés et, lorsque la dissolution est totale, on complète à 200 ml au moyen d'eau distillée.

D'autre part, une solution environ 0,1 M de sulfate cuivrique est préparée en dissolvant 2,5 g du même sulfate pour faire 100 ml; on prélève exactement 5 ml sur les 200 ml de la première solution; on introduit cette prise d'essai dans une fiole avec 250 ml d'eau distillée et un peu de murexide préparée comme indiqué plus loin; On place la solution de sulfate cuivrique 0,1 M dans une burette de 5 ou 10 ml graduée en 0,02 ml et fait couler cette solution goutte à goutte dans la fiole jusqu'au virage de la murexide. Le volume de solution utilisé, multiplié par 39, donne celui à ajouter dans les 195 ml de réactif restant; ceci fait, on complète le tout à 220 ml au moyen d'eau distillée.

Murexide: on sait que les solutions aqueuses de murexide ne sont que très brièvement utilisables[31] et que la solution alcoolique à 70° se décompose lentement;[32] nous avons choisi une solution à 0,15% dans l'éthylène-glycol suivant les recommandations de Brunisholz *et al.*;[33] on peut toutefois remplacer cette solution par un mélange sec avec le chlorure de sodium[34–35] ou avec le sulfate de potassium.[36]

Sulfate cuivrique 0,01 M: 2,5 g de sulfate cuivrique pentahydraté sont dissous dans l'eau distillée de façon à obtenir un litre de solution. Le titre de ce réactif est établi au moyen d'une solution d'E.D.T.A disodique 0,01 M en présence de murexide à un pH compris entre 8 et 10. Nous avons utilisé un poids connu de magnésium pur "dissous" dans l'acide chlorhydrique pour étalonner la solution d'E.D.T.A. avec le Noir Eriochrome comme indicateur et en opérant à un pH voisin de 10.

Eau distillee: nous avons employé une eau distillée fraîchement bouillie pour la préparation des solutions ci-dessus aussi bien que pour la mise en oeuvre de toutes les opérations de la présente technique.

Mode opératoire

Dans une fiole jaugée de 100 ml en verre Pyrex surmontée d'un tube de verre servant de condenseur, placer quelques très petits fragments de verre ou de porcelaine et introduire 10 ml de réactif cuivrique mesurés exactement au moyen d'une pipette; ajouter 10 ml de la solution de glucose à doser mesurés avec la même précision; placer la fiole dans un chauffe-ballon électrique et porter à douce ébullition; maintenir celle-ci pendant 10 min puis ajouter 25 ml d'eau distillée froide par le tube condenseur; refroidir à température ambiante, retirer le tube condenseur et compléter à 100 ml au moyen d'eau distillée; agiter pour homogénéiser et laisser reposer pendant quelques minutes.

Dès que l'oxyde cuivreux s'est déposé, ce qui a lieu très rapidement, prélever exactement 20 ml du liquide surnageant au moyen d'une pipette; les introduire dans une fiole d'Erlenmeyer de 250 ml; ajouter 80 à 100 ml d'eau distillée et une quantité de murexide juste suffisante pour obtenir une légère coloration violacée.

Ajouter la solution de sulfate cuivrique, au moyen d'une burette de 10 ml graduée en 0,02 ml, jusqu'au virage de l'indicateur; ce virage est très brusque et parfaitement net; il a lieu du violacé au vert plus ou moins jaunâtre en passant par une teinte grisâtre paraissant presque incolore lorsque l'indicateur est peu abondant; nous avons choisi cette teinte intermédiaire comme point final de dosage. La solution de sulfate cuivrique n'étant jamais exactement centimolaire, il nous a paru plus commode d'exprimer les mesures en nombre de millimoles d'E.D.T.A. libéré plutôt qu'en volume de réactif utilisé; ce nombre est calculé au moyen de la formule ci-dessous:

$$E = V \times N' \times 5$$

V = nombre de millilitres de solution de sulfate cuivrique utilisé, N′ = molarité exacte de cette solution.

La technique a été experimentée sur des poids de glucose compris entre 5 et 25 mg; les résultat-obtenus correspondent, avec des différences minimes, aux valeurs indiquées par le tableau d'Eschsmann.[14] Ce tableau peut servir au calcul du nombre de mg de glucose présent dans les 10 ml de solution essayée; nous avons remarqué, toutefois, que ce nombre pouvait être calculé, pour les poids compris entre 5 et 25 mg que nous avons essayés, au moyen d'une seule formule que nous donnons ci-après:

$$P = E(5{,}75E + 36{,}1) + 0{,}26.$$

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Résumé—Le glucose peut être dosé par chelatométrie en mesurant la quantité d'E.D.T.A. libéré de son complexe cuivrique après réduction du cuivre II en oxyde cuivreux; la mesure est faite, sans filtration, au moyen d'une solution titrée de sulfate cuivrique en présence de murexide.

Summary—Glucose can be determined chelatometrically by measuring the amount of EDTA liberated from its copper(II) complex after reduction of copper(II) to copper(I) oxide. The EDTA is measured, without filtration, by titration with a standard solution of copper(II) sulphate using Murexide as indicator.

Zusammenfassung—Glucose kann chelatometrisch bestimmt werden durch Messung der EDTA-Menge, die aus ihrem Kupfer(II)-Komplex frei wird, wenn Kupfer(II) zu Kupfer (I)-oxyd reduziert ist. Die EDTA wird ohne Filtration durch Titration mit eingestellter Kupfer(II)-sulfatlösung und Murexid als Indikator bestimmt.

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LETTERS TO THE EDITOR

Determination of sulphate with barium chloranilate

A recent paper by Agterdenbos and Martinius[1] leaves the impression with the reader that the widely used spectrophotometric method for determining sulphate with barium chloranilate is of limited usefulness. The conclusions drawn by these authors were based on a mathematical treatment of the equilibria existing in solutions containing extremely small amounts of sulphate. The absorbance-concentration relationship for the reaction:

$$\text{barium chloranilate} + \text{sulphate} \rightarrow \text{acid chloranilate} + \text{barium sulphate}$$

becomes non-linear at low concentrations of sulphate because of the solubility of the barium salts and the dissociation of the acid, and because of the changes in the ionic strength.

These problems were considered by the developers of the method, and they were discussed in a paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in March 1957.[2] Because the deviations from linearity were caused by easily understood relationships discussed in elementary textbooks of physical chemistry, this discussion was omitted from the publication.[3]

Examination of the equations presented by Agterdenbos and Martinius reveals that the deviations from linearity caused by solubility and equilibria relationships are significant only below about 0·2 μg/ml (0·2 ppm) of sulphate if 4-cm cells are used, or below 0·05 ppm in the more commonly used 1-cm cells. This concentration is well below the range of sulphate concentrations for which the method is used. However, Fig. 2 of their paper clearly shows that the method can be used at a concentration of 0·2 μg/ml in 4-cm cells.

The results in Table IV of the paper purport to show the effect of the ionic strength on the error obtained in the measurement of absorbance. However, no direct relationship between ionic strength and the magnitude of the error can be obtained from the results in this table, other than the well-known positive error at high ionic strengths. Furthermore, the spread in the experimental values in Fig. 2 suggests that the error of one of the authors' single measurements may be as high as ±0·04 absorbance unit.

Several criticisms may be offered about the authors' experimental results and their theoretical treatment. The method used by them to prepare barium chloranilate (*i.e.*, by adding an excess of chloranilic acid to barium chloride solution) will surely produce a compound which is contaminated with chloranilic acid, so that high, inconsistent blanks will be obtained. They also gave no reason for using urotropine as a buffer rather than the highly satisfactory acetic acid-sodium acetate mixture.[4] Furthermore, the absorbance of blank solutions of barium chloranilate was not given by the authors. All of the commerical and experimental samples of barium chloranilate examined by the developers of the method gave absorbances of at least 0·6 in 1-cm cells at pH 4·5 at 332 mμ. Because absorbance of the blank increases as the pH increases, the blank solutions studied by the authors in 4-cm cells must have had extremely high absorbances.

The authors infer that previous workers have assumed that the calibration curve passes through the origin. Careful examination of Fig. 1 of reference 4 and the slides presented in reference 3 reveals that the developers of the method did not represent the calibration curve in this manner. Also, the authors have incorrectly neglected the contribution of the acid chloranilate ion to the total absorbance of the solution.

In conclusion, the authors have correctly described some obvious but trivial limitations of the spectrophotometric method for determining sulphate with barium chloranilate These limitations should be apparent to chemists familiar with chemical equilibrium theory. They may be important for other exchange reactions used in analytical chemistry. The spectrophotometric method for sulphate is useful for most systems, and the calibration curve is linear in the practical range of absorbance.

J. E. BARNEY, II

Midwest Research Institute
425 *Volker Boulevard*
Kansas City, Missouri, U.S.A.
16 *October* 1964

REFERENCES

[1] J. Agterdenbos and N. Martinius, *Talanta*, 1964, **11**, 878.

[2] J. E. Barney, II and R. J. Bertolacini, paper presented at the Eighth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1957.

[3] J. E. Barney, II and R. J. Bertolacini, *Analyt. Chem.*, 1958, **30**, 202.

[4] R. W. Klipp and J. E. Barney, II, *ibid.*, 1959, **31**, 596.

SIR,

When we saw Dr. Barney's letter[1] we were appreciative that he, who should be a specialist in this respect because he was the first investigator who applied barium chloranilate to the determination of small amounts of sulphate, had read our paper[2] and given some comments on our work. After we had read his letter, however, it seemed useful for us to reply to his comments.

1. Dr. Barney suggests that the results of our calculations are so self-evident that it is unnecessary to publish them. We cannot agree with this view. Of course, qualitatively, they are self-evident, but they are so in many analytical determinations where equilibria play an important role. Fortunately, however, the magnitude of the effect is not large enough in many cases to cause a significant change of the calibration curve from linearity and significant influence of ionic strength on the curve. In the problem we studied, the magnitude of the deviations proved to be sufficiently large to be discussed quantitatively. We believe that our calculations give a good insight into the scope and limitations of the method. We are afraid that some error is involved in Dr. Barney's statement that some figures from his references 3 and 4 give information on the calibration curves he obtained. We regret that we could not find any information of the kind suggested in these references. (Unfortunately no report was available of the lecture. From the footnote to his paper in reference 3 and from our reference 1 in this letter we conclude, however, that his reference 3 should be regarded largely as a written report of this lecture.)
2. Dr. Barney's conclusions on the error made in the determination of the blank values in our Table IV are not well founded for at least two reasons. Firstly, he makes his conclusions from the values found in our Fig. 2. However, the experiments made to obtain the values in this figure were much more complicated than those used to obtain the values of Table IV. Secondly, the value of 0·04 he gives for the error in the absorbance is rather pessimistic. Our Fig. 2 clearly shows that the range found at the highest concentration level is about 0·05 or 0·06 extinction unit, obtained from 6 or 7 determinations. This gives a most probable value of about 0·02 for the value of the standard deviation. An error of 0·04 may, of course, be found, but it may be expected only in a few cases, even in the more complicated experiments.
3. We cannot agree with Dr. Barney's conclusions on the preparation of the reagent. The fact that we did not obtain satisfactory results when it was prepared according to Dr. Barney's directions (with a *large* excess of barium) may arise from slight differences in the preparation procedure. Without further experimental evidence, however, we cannot see that our procedure (using a *small* excess of chloranilate) should surely give rise to less satisfactory results than Dr. Barney's procedure, because an excess of barium may give inconsistently *low* results. In fact, our investigation included a large variation in the amount of reagent used for determination of the blank. No influence of such a variation on the blank value was found and it was, therefore, concluded that the contamination of our reagent was not important.

   Dr. Barney's conclusions on the value of our blanks are badly founded by his comparison with his own values, because we clearly showed the influence of alcohol concentration and ionic strength and both were quite different in his and in our experiments. In fact, our value was about 0·88 in a 4-cm cell, which seems favourable when compared with his value of at least 0·6 in a 1-cm cell!
4. Regarding the use of urotropine, we prefer the use of this buffer to acetate because it may be assumed that under our experimental conditions it has a lower ionic strength at the same buffering capacity.
5. From the values we cited for the dissociation constants of chloranilic acid in water ($pK_1 = 0{\cdot}85$, $pK_2 = 3{\cdot}18$), it follows that no significant contribution of the acid chloranilate may be expected in this solvent at about pH 5·2. It is difficult to predict the apparent pH required to fulfil this condition in about 70% alcohol, but the fact that a small change in apparent pH did not influence the value of ε (page 881 of our paper) makes it probable that no significant amount of acid chloranilate were present in our experiments.
6. Dr. Barney suggests that the results of our Table IV should show the effect of ionic strength on the error. However, it should be clear from both this table and page 882 that it only gives the

relationship between ionic strength and extinction. The values given indicate that theory and experiment agree well, and Table IV on page 881 gives the information which Dr. Barney wishes for some practical conditions!

7. We do not believe that in practice the problem of the determination of small amounts of sulphate is restricted to samples with low and well known ionic composition. We cannot, therefore, agree with his conclusion on the usefulness of the method. In samples with favourable ionic composition, however, the method is useful (as we said on page 884 of our paper).

Analytisch Chemisch Laboratorium
der Rijksuniversiteit te Utrecht
Croesestraat 77a
Utrecht, Netherlands.
15 *January* 1965

J. Agterdenbos
N. Martinius

REFERENCES

[1] J. E. Barney, II, *Talanta*, 1965, **12**, 425.
[2] J. Agterdenbos and N. Martinius, *ibid.*, 1964, **11**, 875.

Concerning a certain international experiment

Sir,

In a paper by Cook *et al.*, which appeared in this journal,[1] results were given of an international comparison of analytical methods, designed to show the accuracy and precision of some techniques of routine trace analysis for nuclear materials. This interesting and, in its way, original work was arranged in order to compare the analytical results of some relatively common materials (aqueous solutions containing the nitrate salts of copper, chromium, manganese and mercury), obtained by four different methods in nine representative laboratories in various countries. The extensive and important material accumulated during the investigation has been subjected by the authors to an elementary statistical treatment:[2] in particular, mean values were calculated, also standard deviations and confidence limits of single determinations and of the average results; all this data was presented in the paper as tables and figures. The reduced data shows clearly that some of the methods compared are preferable from the point of view of precision and accuracy. In this way, the importance of the work carried out by the co-operation of international research workers is obvious and has been pointed out more than once[3,4] in reviews.

However, in our opinion, the method chosen by the authors[1] of presenting the results of the research is not the best, because the points of many important conclusions of the work are not made or remain obscure. It is necessary to point out separately that the vast experimental material accumulated by the international researches (551 results in all) could serve as a source of far greater extent and variety of information (or international interest!), than the information which the reader can find in the paper in question. In particular, it does not seem to be quite correct to incorporate results (for their subsequent statistical treatment), some of which may possibly not appertain to the same population. Besides, when dealing with samples of analysed results of different sizes (n) and different origins, it seems that for the sake of clarity the values of standards (s) should be given rather than confidence limits (ts), *etc.*

Most probably in the treatment of such statistical material a multifactor analysis of variance would be very useful.[5–12] Such mathematical treatment would allow the clear revelation of errors of repeatability and reproducibility, as well as errors which are inherent in the different methods within the same technique, *etc.* Also, it would be useful to clear up these questions whether the accumulated results are submitted to the law of normal distribution, or whether they are to fulfil some other statistical procedure for "squeezing out" the maximum information from the results.

Undoubtedly, it would hardly be possible for each reader to present his own "account" to the authors and to satisfy all claims of this type. That is why we should not judge the authors severely and this is not the purpose of our letter. Slips are almost inevitable in any new matter, and to criticise is always somewhat easier than to do the job.

We consider it expedient that the authors of the article refer to the accumulated material once more and publish it in this journal as tables of all (without exception) initial numerical data. This would allow the specialist, possessing different methods of statistical treatment of experimental results and having different interests, to treat the material according to his own judgement—*lege artis*—and to extract for himself the maximum use of the information. We clearly recognise that these deliberations are rather late, but nevertheless "Better late than never!" Briefly: *Numerus fundamentum rei publicae.*

Sincere thanks are expressed to our friends and colleagues, Miss K. Moloshnikova for her kindly assistance, Dr. I. V. Krivoshei for interesting evening discussions and Mrs. H. G. Klausnitzer for the English translation.

A. B. Blank
Rudolph Alexander Geitz

Department of Analytical Chemistry
A.M. Gorky Khar'kov State University
Ukraine, U.S.S.R.
22 *October* 1964

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SIR,

The letter of Drs. Blank and Geitz raises, apart from specific points related to our paper, a very general problem of science today, and that is the ever increasing number of scientific papers submitted for publication each year. Editors of journals, faced with this problem, exercise the right to reduce the length of a submission, if, in their opinion, unnecessary or unsuitable material is included. In our case, the preliminary report which included all results was considered by the Editor-in-Chief, who, however, preferred not to publish individual values which made up laboratory averages. We did not press this point further because we believe that it is normal scientific practice for an interested worker to apply to authors of published papers for further clarification or additional data, which is normally freely given. In fact, as we knew that further statistical data could be derived from the collected results, we anticipated that such requests might be made; we were and still are very willing to supply all the data (except the identification of the individual laboratories) to anyone wishing it.*

On the specific points raised by Drs. Blank and Geitz we comment as follows.

1. The statistical treatment given in the paper was considered by us to be sufficient for our purposes, which was to obtain an estimate, in a comparatively simple analytical situation, of the relative value of the techniques as they are normally performed in a routine laboratory. It was hoped that the information obtained on these general aspects would be useful to analytical chemists in their everyday work and we believe this was so.

2. We are aware that the application of more elaborate statistical techniques might reveal other properties of the data, but we decided to limit the treatment to aspects which we considered of more general interest to the chemical profession and which could be put into a paper of reasonable length. Multifactor variance analysis, for instance, would have permitted the isolation of different causes of divergence in results among laboratories and perhaps to rate them according to some quality criterium, but this was not the purpose of the work. Moreover, we felt that the quite large assortment of methods, elements, laboratories, operators, standards and other conditions would cause such analysis to be of doubtful general chemical value.

3. The use of ts instead of s in our expressions for the mean values allowed all data of different origin to be put on the same footing, considering that some of the means were derived from sets containing only 2 or 3 results, against the average of 5. It is obvious that ts contains not only the information on precision given by s but also the intrinsic quality of this information. We could have assigned a weight to the different sets, but we thought that the use of ts gave a more objective basis.

4. It should also be pointed out that no results were rejected, although we believed that systematic errors were included. In this respect our assumption was that the random distribution of systematic errors could be treated mathematically as if it were a proper distribution of random errors because the causes of these biases were not known.

5. Finally, we wish to point out that our treatment is only *one* of those possible and claim in its favour only that it filled our needs at the time of writing and that its results were not of merely mathematical interest but proved to be useful to chemists working in the field.

G. B. Cook*
M. B. A. Crespi†
J. Minczewski‡

International Atomic Energy Agency
Seibersdorf Laboratory, Seibersdorf
Niederösterreich, Austria.
15 *February* 1965

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* Please apply to G. B. Cook at address shown.

† Present address: Comision Nacional de Energia Atomica, Buenos Aires, Argentina.

‡ Present address: Institute of Nuclear Research, Warsaw, Poland.

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NOTICES

AUSTRALIA

Monday 31 *May–Wednesday* 2 *June* 1965: **Fifth Australian Spectroscopy Conference:** *Australian Academy of Sciences.* Perth, W. Australia.

CANADA

Wednesday–Friday 26–28 *May* 1965: **Eleventh National ISA Analysis Instrumentation Symposium,** jointly with **Sixth National ISA Chemical and Petroleum Instrumentation Symposium with Section Exhibit.** Sheraton-Mount Royal Hotel, Montreal.

Monday–Wednesday 4–6 *October* 1965: Meeting on **Industrial Organic Analysis:** *Chemical Institute of Canada, Analytical Chemistry Division.* Drawbridge Inn, Sarnia, Ontario.

Sessions are being planned in: Trends in Industrial Analysis; Advances in Analytical Spectroscopy; Characterisation of Polymers. There will be three additional sessions, one of which will be devoted to Gas Chromatography.

Further information may be obtained from R. M. SMALL, Research Department, Polymer Corporation Ltd., Sarnia, Ontario, Canada.

CZECHOSLOVAKIA

IV. Internationaler Polarographischer Kursus

In der Zeit vom 6.9. bis 18.9.1965 veranstaltet das Institut für physikalische Chemie der Karlsuniversität und das Polarographische Institut der Tschechoslowakischen Akademie der Wissenschaften einen Lehrgang in Polarographie. Dieser Kursus besteht aus Vorlesungen über die Grundlagen der Polarographie, die in deutscher Sprache abgehalten werden, und einem entsprechenden Praktikum. Der Lehrgang ist für Hochschulabsolventen gedacht, spezielle Vorkenntnisse der Polarographie sind jedoch nicht Bedingung. Die Zahl der Teilnehmer wird auf 20 begrenzt. Dieser Lehrgang wird vorbereitet unter Schirmherrschaft von Professor Dr. J. Heyrovský, die Vorlesungen und das Praktikum liegen in den Händen von Fachkräften der Karlsuniversität und des Polarographischen Institutes. Die Teilnahmgebühr beträgt Kčs 500.—einschliesslich eines Ausfluges in die Umgebung Prags und eines gemeinsamen Abendessens am Abschlusstage des Lehrganges, Unterbringung in Studentenheimen zu mässigen Preisen wird gewährleistet.

Vorläufige Anmeldungen mit Angabe von Titel, Name und Adresse sind an das Institut für physikalische Chemie der Karlsuniversität, Prag 2, Albertov 2030, bis spätestens 1. Juni 1965 zu richten.

DEUTSCHE DEMOKRATISCHE REPUBLIK

Die Unterkommission für Gas-Chromatographie veranstaltet im Mai 1965 in Berlin ihr

V. Symposium über Gas-Chromatographie

Wegen einer Überschneidung hat sich der in früheren Ankündigungen mitgeteilte Termin als ungünstig erwiesen. Die Tagung wurde deshalb auf die Zeit

vom 18. bis 21. Mai 1965

verlegt

Das Symposium steht nicht unter einem speziellen Thema, sondern es sollen gleichermaßen
- die Theorie der Trennung,
- das Verhalten der flüssig-stationären Phase,
- Probleme der Adsorption,
- Fragen der Detektion und Auswertung,
- methodische Arbeiten und
- spezielle Anwendungen der Gas-Chromatographie

behandelt werden. Diese Absicht spiegelt sich in den bereits vorliegenden und weiter unten aufgeführten Vortragsmeldungen wider.

In Anbetracht der zu erwartenden starken ausländischen Beteiligung und der Fülle des vorliegenden Materials scheint es angezeigt, dem V. Symposium über Gas-Chromatographie den Charakter einer Diskussionstagung zu geben. Es sollen daher alle Beiträge als Manuskript gedruckt den Tagungsteilnehmern vor Beginn der Veranstaltung zugesandt werden.

Eingegangene Vortragsmeldungen

Zur Theorie der Trennung

G. SCHAY

Zum gegenwärtigen Stand der Theorie der Gas-Chromatographie (Hauptvortrag)

O. GRUBNER und E. KUČERA

Ergebnisse der Theorie der statischen Momente und ihre Bedeutung für Gas-Chromatographie

A. PETHÖ

Bemerkungen zum Begriff der Trennstufe

M. S. WIGDERGAUS

Über einige Fragen der Theorie der Gas-Chromatographie

Die flüssig-stationäre Phase

H. KELKER

Neue Ergebnisse mit flüssig-kristallinen Schmelzen als stationäre Phasen (Hauptvortrag)

M. KREJČI, H. DUBSKY, M. RUSEK und K. TESAŘIK

Theoretische Aspekte der Benetzung von Trägern durch Trennflüssigkeit in der Gas-Chromatographie

C. KEHRER, H. G. STRUPPE und E. LEIBNITZ

Zum Einsatz polarer Trennflüssigkeiten in Kapillarsäulen

W. ECKNIG, H. ROTZSCHE und H. KRIEGSMANN

Über Zwischenmolekularkräfte und Auswahl von Trennflüssigkeiten

E. A. KRUGLOW, K. M. WEIßBERG und S. I. ABRAMOWITSCH

Gebrauch von Pentaerythritäthern in der Gas-Chromatographie als stationäre Phase

F. FALK

Verwendung von Äthylenglykol-γ-Ketopimilatpolyester als GC-Flüssigphase in der Fettchemie

Fragen der Detektion und Auswertung

G. SCHOMBURG

Moderne Detektoren für die Gas-Chromatographie (Hauptvortrag)

O. PIRINGER und E. TĂTARU

Der Elektrolytleitfähigkeitsdetektor, Konstruktion, Arbeitsweise und Anwendung

H. DUBSKÝ

Ein Beitrag zu den in der Gas-Chromatographie angewandten Verbrennungsmethoden

J. LEONHARDT und H.-K. BOTHE

Der Nachweis anorganischer Gase mit dem Argon-Ionisationsdetektor

G. GNAUCK und H. SCHÖN

Neue Ergebnisse des Nachweises von permanenten Gasen mit β-Strahlen-Ionisationsdetektoren

S. MATOUŠEK

Argondetektor mit zwei Ausgangssignalen für den Anschluß einer automatischen Auswerteeinrichtung

H.-K. BOTHE, H. HILBIG und P. POPP

Die Identifizierung gas-chromatographisch getrennter Substanzen auf Grund ihres Elektronenanlagerungsvermögens

M. WURST

Die gas-chromatographische Analyse von Organosiliciumverbindungen unter Verwendung einer Gasdichtewaage

G. GARZÓ u. a.

Die Anwendung des Flammenionisationsdetektors bei der Analyse von siliciumorganischen Verbindungen

H. HOLZHÄUSER

Studien zur quantitativen Auswertung gas-chromatographischer Analysen

Z. TYPLT

Auswerteeinrichtung für schnellaufende Gas-Chromatographie

G. SCHUBERT

Ein volltransistorisiertes Bausteinsystem eines Schwingkondensatorverstärkers und dessen Einsatzmöglichkeiten in der Gas-Chromatographie

B. PETZELT

Neuer Universalchromatograph in Bausteinweise

V. KUSKY und V. PROCHAZKA

Erfahrungen mit der automatischen Betriebschromatographie für die Analyse von gasförmigen und flüssigen Produkten

E. GRIMM

Über Prozeßchromatographie

Beiträge zur Methodik

G. GUIOCHON

Temperaturprogrammierte Analyse mit Kapillarsäulen (Hauptvortrag)

A. A. SHUCHOWIZKI

Betrachtung zur Vakanto- und trägergaslosen Chromatographie

J. NOVÁK, V. VAŠÁK und J. JANÁK

Eine neue chromatographische Methode für die Bestimmung der Konzentration von Spurenkomponenten in Gasen

J. FRANC, F. MIKEŠ und M. PIKEŠ

Identifizierung organischer Substanzen mit Hilfe der Gas-Chromatographie an Hand chromatographischer Septren

K. HÖPPNER, U. PRÖSCH und H.-J. ZÖPFL

Präparative Gas-Chromatographie von Methyl- und Äthylzinnverbindungen

M. ŠINGLIAR

Identifizierung organischer Stoffe durch Hydrierung

W. G. BERESKIN und A. T. SWIATOSCHENKO

Untersuchungen an gefüllten Kapillarsäulen

K. M. WEIßBERG u. a.

Untersuchung der Zusammensetzung der bicyclischen aromatischen Kohlenwasserstoffe mit Hilfe der Gas-Chromatographie und Molekularspektroskopie

F. Lange, J. Erpenbeck, U. Prösch und H.-J. Zöpfl

Gas-chromatographische Untersuchuungen über die präparative Gastrennung durch Zirkulardiffusion

Spezielle Anwendungen

M. Filipescu u. a.

Die Anwendung der Gas-Chromatographie zur Feststellung des absoluten Alters von Gesteinen nach der Ar-K-Methode

H. Sackmann, A. Losse und J. Wilke

Beitrag zur Gas-Chromatographie der Tetrachloride von Silicium, Zinn und Titan

K. Tesařik

Die Bestimmung der Spurenkonzentrationen von COS und CS_2 in der Atmosphäre

H. W. Schulze und H.-K. Bothe

Gas-Chromatographie radioaktiv markierter Substanzen

D. A. Wiachirew

Qualitative und quantitative gas-chromatographische Untersuchung von Verunreinigungen in Methylmetacrylat und in Methylacrylat

M. Peter und L. Torkos

Gas-Chromatographie Analyse der bei Aromatengewinnungsversuchen entstandenen Extrakte

N. I. Lulowa u. a.

Gas-chromatographische Untersuchungen des durch katalytische Hochtemperaturcrackung erhaltenen Benzins

J. Cabal

Analyse hochsiedender paraffinischer Produkte

A. G. Werestschagin

Identifikation und quantitative Bestimmung höherer Fettsäuren durch Verteilungs-Gas-Chromatographie

K. Rühlmann und G. Michael

Neue Versuche zur Gas-Chromatographie der Aminosäure-Silylderivate

Probleme der Sorption und Modifizierung

A. V. Kiselev

Die Rolle der geometrischen und chemischen Faktoren der Struktur der Adsorbentien und Träger für die Gas-Chromatographie (Hauptvortrag)

D. A. Wiachirew

Adsorption und gas-chromatographische Eigenschaften des mit Kalilauge behandelten Kieselgels und dessen Verwendung zur Analyse von Kohlenwasserstoffgemischen

N. P. Dimov

Chromatographie der leichten Gase auf metallersetzbaren Silikagelen

K. I. Sakodynski

Präparative Trennung auf modifizierten Adsorbenten

G. Gnauck

Beitrag zur Anwendung von porösen Gläsern in der Gas-Chromatographie

K. D. Stscherbakowa

Einfluß der Dehydroxylierung der Oberfläche breitporiger Silikagele auf das chemische Modifizieren und die Gas-Chromatographie

I. A. Mussaew und P. I. Sanin

Untersucung fester Träger für die Gas-Chromatographie

O. Grubner und R. Vespalec

Die Messung der Sorptionsisothermen von organischen Dämpfen durch eine modifizierte Methode von Glueckauf

H. Beyer und G. Schay

Bestimmung von Adsorptionsisothermen und Oberflächengrößen nach einer modifizierten Sorptiometermethode

E. Smolková, O. Grubner und L. Feltl

Bestimmung kleiner Oberflächen von pulverförmigen Stoffen mit der Methode der Wärmedesorption

O. Piringer und E. Tătaru

Die Anwendung der Gas-Chromatographie zu Chemisorptionsuntersuchungen des Wasserstoffs an Metallen

R. Komers

Untersuchung der Sorption von organischen Verbindungen durch eine dynamische Pulsmethode

L. Feltl, O. Grubner und E. Smolková

Messung der Sorption von organischen Dämpfen an pulverförmigen porosen Sorbenten durch die Methode der frontalen Gas-Chromatographie

Weitere das Symposium betreffende Anfragen richten Sie bitte an die

Unterkommission für Gas-Chromatographie—Sekretariat
705 LEIPZIG, Permoserstraße 15, Deutsche Demokratische Republik

FRANCE

Vendredi 7 *mai* 1965: Journée de Chimie Analytique dans le cadre de l'Assemblée annuelle de la Sociéte Chimique.

Mardi 11 *mai* 1965: **Le phénomène de fluorescence et ses applications analytiques,** par M. R. Bourdon, à 17 h 45, à la Faculté de Pharmacie de Paris.

Mardi 25 *mai* 1965: **L'analyse instrumentale: développements récents. Perspective d'avenir,** par M. J. C. Lefebvre, à 17 h 45, à la Faculte de Pharmacie de Paris.

UNITED KINGDOM

Friday–Saturday 9–10 *April* 1965: **Infrared Spectroscopy:** *Society for Analytical Chemistry, Microchemical Methods Group* and *Special Techniques Group.* University of Sussex, Falmer, Brighton.

The programme is as follows:

Friday Evening

Some Advances and Trends in Infrared Spectroscopy.	D. M. W. Anderson
Study of Chelate Compounds by Infrared Spectroscopy.	R. J. Magee
Infrared Spectroscopy applied to Very Small Quantities.	H. A. Willis

Saturday Morning

Infrared Spectra of Inorganic Materials.	D. F. Evans
Application of Long-path (40*m*) *Gas Cells to Analysis of Atmospheric Pollution.*	L. C. Thomas
Infrared Analysis by Attenuated Total Reflectance.	N. A. Puttnam

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Wednesday 14 *April* 1965: **Commercial Absorption Apparatus Meeting:** *Society for Analytical Chemistry, Atomic-Absorption Spectroscopy Group.* Sheffield College of Technology, Pond Street, Sheffield 1.

There will be a demonstration of commercial apparatus starting at 10.00 a.m. followed by a discussion at 7.00 p.m.

Tuesday 4 *May* 1965: **Some Problems in Water Conservation,** F. Law and L. R. Bays: *Society for Analytical Chemistry, North of England Section* and *Royal Institute of Chemistry, North Lancashire Section.* Harris Technical College, Preston, 7.15 p.m.

Wednesday 5 *May* 1965: Contributions from Research Workers in Universities and Colleges of Advanced Technology. Bradford Institute of Technology, 2.30 p.m.

Wednesday 26 *May* 1965: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemical Methods Group. The Feathers,* Tudor Street, London E.C.4, 6.30 p.m.

Wednesday 30 *March* 1966: **Symposium on Nuclear Magnetic Resonance and Electron Spin Resonance:** *Society for Analytical Chemistry, Midlands Section* and *Special Techniques Group; Royal Institute of Chemistry, Birmingham and Midlands Section; Society for Chemical Industry, Midlands Section.* University of Birmingham.

Anyone wishing to attend the meeting or to receive further information should communicate with Mr. M. L. Richardson, John and E. Sturge Ltd., Lifford Lane, Kings Norton, Birmingham 30.

Tuesday–Thursday 14–16 *September* 1966: **Conference on Particle Size Analysis.** Loughborough College of Technology, Leicestershire.

Papers and discussions will describe original work in the field.

At the *Annual General Meeting* of the **Society for Analytical Chemistry,** held on Friday, 5 March, 1965, the following were elected Officers and Members of Council for the forthcoming year:

President: A. A. Smales
Past Presidents serving on Council: A. J. Amos, R. C. Chirnside, D. C. Garratt, J. H. Hamence
Vice-Presidents: A. G. Jones, C. Whalley
Hon. Treasurer: D. T. Lewis
Hon. Secretary: S. A. Price
Hon. Assistant Secretaries: B. S. Cooper (programmes), D. W. Wilson

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At the *Annual General Meeting* of the **Midlands Section** of the **Society for Analytical Chemistry,** held on Friday, 12 March, 1965, the following were elected Officers for the forthcoming year:

Chairman: W. T. Elwell
Vice-Chairman: H. E. Brookes
Hon. Secretary: M. L. Richardson, John and E. Sturge Ltd., Lifford Lane, Kings Norton, Birmingham 30
Hon. Treasurer: G. Ingram
Hon. Assistant Secretary: R. Adkins

British Standards Institution has announced the following *New British Standards:—B.S.* 3727: *Methods for the analysis of nickel for use in electronic tubes and valves: Part* 11: 1965: *Determination of silicon* 0.001–0.020% *(photometric method). Part* 13: 1965: *Determination of titanium (photometric method).* For each part of the reagents required, the test procedure and the necessary details are specified for each determination. (*Price:* 4s. each)

The following *Amendment Slips* are also announced:

B.S. 1673: *Methods of testing raw rubber and unvulcanised compounded rubber: Part* 2: 1954: *Methods of chemical analysis. Amendment No.* 5. *PD* 5408.

B.S. 1902: *Methods for testing refractory materials: Part* 2 *A:* 1964: *Chemical analysis of high silica and aluminosilicate materials. Amendment No.* 1. *PD* 5427.

B.S. 3210: 1960: *Methods for the analysis of water-soluble coal-tar dyes permitted for use in foods. Amendment No.* 1. *PD* 5430.

UNITED STATES OF AMERICA

Tuesday–Friday 4–7 *May* 1965: **Spring Meeting,** including **Symposium on Physical and Chemical Testing:** *American Chemical Society, Division of Rubber Chemistry.* Fontainebleau Hotel, Miami Beach, Fla.

Wednesday–Saturday 5–8 *May* 1965: **Sixth International Pulp and Paper Instrumentation Symposium:** *Instrument Society of America.* Hotel Northland, Green Bay, Wis.

Thursday–Saturday 6–8 *May* 1965: **Conference on Purification of Materials.** Waldorf Astoria Hotel, New York City.

Wednesday–Thursday 12–13 *May* 1965: **National Forum on Control of Water Quality:** *American Society for Testing and Materials.* ASTM Headquarters, Philadelphia, Pa.

Sunday–Friday 16–21 *May* 1965: **Thirteenth Annual Conference on Mass Spectrometry and Allied Topics:** *American Society for Testing and Materials, Committee E-*14 *on Mass Spectrometry.* Sheraton-Jefferson Hotel, St. Louis, Missouri [see *Talanta,* 1964, **11**(12) ii].

Wednesday–Friday 25–27 *August* 1965: **Fourteenth Annual Conference on Applications of X-Ray Analysis:** *Metallurgy Division, Denver Research Institute, University of Denver.* Albany Hotel, Denver, Colorado.

Sessions are planned on X-Ray Diffraction, -Emission Spectroscopy, -Microprobe Analysis, -Absorption and Microscopy, -Instrumentation, -Topography and -Small Angle Scattering. There will be special sessions on Soft X-Rays and Effects of Chemical Combination on X-Ray Spectra.

Papers are invited, of which titles and abstracts are due on 16 April.

Thursday–Friday 3–4 *February* 1966: **First Middle Atlantic Regional Meeting:** *American Chemical Society.* Sheraton Hotel, Philadelphia, Pa.

This Meeting will be the first of an annual series, replacing the former Delaware Valley and Metropolitan Regional Meetings. The cosponsoring ACS local sections are Delaware, Lehigh Valley, Monmouth County, New York, North Jersey, Philadelphia, Princeton, South-Eastern Pennsylvania, South Jersey and Trenton.

There will be nine scientific divisions for the presentation of papers, including one on *Analytical Chemistry* (Chairman: Mr. O. I. Milner, Socony Mobil Oil Co.). Further information may be obtained from Dr. Walter Clavan, Pennsalt Chemicals Corporation, Technological Center, King of Prussia, Penna. 19406.

Monday–Friday 9–13 *August* 1965: **Gordon Research Conference on Analytical Chemistry.** New Hampton School, New Hampton, New Hampshire.

The programme is as follows:

Monday, 9 *August*	
Applications of NMR to Polymer Structure Determination.	W. M. Ritchey
Cation-Sensitive Electrodes: Theory and Practice.	G. A. Rechnitz
Tuesday, 10 *August*	
Applications of Differential Thermal Analysis to Polymers.	B. Wunderlich
General Applications of Differential Scanning Calorimetry.	A. P. Gray
Applications of Differential Thermal Analysis to Non-polymeric Systems.	P. D. Garn
Wednesday, 11 *August*	
Modernisation of Microanalytical Methods.	H. Malissa
Use of Group Frequency Shifts in Interpreting Infrared Spectra.	W. J. Potts
Applications of Infrared Spectroscopy to Bio-Medical Analytical Problems.	D. Erley
Thursday, 12 *August*	
Advances in Spark Source Mass Spectrometry.	A. J. Ahearn
Open Session.	
Friday, 13 *August*	
Analytical Problems in Drug Metabolism Studies.	A. J. Glazko

Further information may be obtained from Dr. W. George Parks, University of Rhode Island, Kingston, Rhode Island.

Talanta, 1965, Vol. 12, p. viii. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Reduction of alkyl disulphides with triphenylphosphine: RAY E. HUMPHREY, AVIS L. MCCRARY and RODNEY M. WEBB. (29 *January* 1965)

Amperometry with two polarisable electrodes—VI: Determination of copper by EDTA titration: J. VORLÍČEK and F. VYDRA. (1 *February* 1965)

Massanalytische bestimmung von lanthan mit natriumwolframat in anwesenheit von adsorptionsindicatoren: WIKTOR WAWRZYCZEK and ALINA BUKOWSKA. (2 *February* 1965)

Determination of deactivated olefines on the submicro scale: R. BELCHER and B. FLEET. (4 *February* 1965)

Separation of zirconium-95, 97 and niobium-95, 97 from uranium fission products by an extraction method using 8-hydroxyquinoline: K. MOTOJIMA, H. HASHITANI, S. BANDO and HIDEYO YOSHIDA. (5 *February* 1965)

Spectrophotometric determination of platinum after extraction of the chloro-stannous complex by high molecular weight amines: M. A. KHATTAK and R. J. MAGEE. (8 *February* 1965)

Spectrophotometric determination of minute amounts of lanthanum with Xylenol Orange: V. SVOBODA and V. CHROMÝ. (8 *February* 1965)

Column and thin-layer chromatographic separation of polynuclear ring carbonyl compounds: EUGENE SAWICKI, THOMAS W. STANLEY and WALTER C. ELBERT. (11 *February* 1965)

Coprecipitation of iron(III) and zinc ions with aluminium tris-(8-hydroxyquinolate): T. H. BAILEY and S. J. LYLE. (12 *February* 1965)

Spectrophotometric determination of palladium with pyridine-2-aldehyde-2-pyridylhydrazone: C. F. BELL and D. R. ROSE. (12 *February* 1965)

Concerning a certain international experiment: G. B. COOK, M. B. A. CREPSI and J. MINCZEWSKI. (15 *February* 1965)

Extraction of thallium(III) from hydrochloric acid solutions with fusel oil phosphate (FOP): T. N. SRIVASTAVA and D. C. RUPAINWAR. (17 *February* 1965)

Measurement of nitrogen in uranium-plutonium dioxides: V. M. SINCLAIR, W. DAVIES and K. R. MELHUISH. (17 *February* 1965)

Analytical methods in non-aqueous media—II: Determination of weak acids: LASZLO LEGRADI. (18 *February* 1965)

Thermoanalytical properties of analytical grade reagents—III: Rubidium salts: L. ERDEY, G. LIPTAY and S. GÁL. (19 *February* 1965)

Spectrophotometric determination of niobium(V) with Bromopyrogallol Red: R. BELCHER, T. V. RAMAKRISHNA and T. S. WEST. (19 *February* 1965)

Interlingua: J. HALL. (22 *February* 1965)

Amperometry with two polarisable electrodes—VII: Chelometric determination of indium by EDTA-titration: F. VYDRA and J. VORLÍČEK. (22 *February* 1965)

Amperometry with two polarisable electrodes—IX: Determination of calcium and magnesium by EDTA-titration: F. VYDRA and J. VORLÍČEK. (22 *February* 1965)

Spectrophotometric determination of copper and nickel in presence of each other—I: V. M. BHUCHAR. (25 *February* 1965)

Spectrophotometric determination of copper, nickel and iron in presence of one another, and its application to the analysis of cupro-nickel alloys—II: V. M. BHUCHAR and (Mrs.) PADMA NARAYAN. (25 *February* 1965)

Determination of traces of platinum in samples of palladium by neutron-activation analysis: D. F. C. MORRIS and R. A. KILLICK. (26 *February* 1965)

Talanta, 1965, Vol. 12, pp. ix to x. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Molecular Complexes in Organic Chemistry: Lawrence J. Andrews and Raymond M. Keefer. Holden-Day, Inc., San Francisco, London, Amsterdam, 1964, Pp. 196. $8.75.

General considerations: Types of donors, Types of acceptors, Occlusion compounds, The bond between complex components; Spectra of complexes: Visible and ultraviolet spectra, Emission spectra, Infrared spectra; Complex geometry: The application of NMR spectroscopy in structure determination, Crystal structures of complexes, Paracyclophane complexes, Polysaccharide-iodine complexes; Stabilities of complexes in solution: Methods of investigation, Equilibrium constants for complex formation, Thermodynamic constants for complex formation; Electrical and magnetic phenomena associated with complex formation: Dipole moments of complexes, Conductivities of complexes, Paramagnetism in complexes; The functions of complexes in organic chemistry: Practical separation procedures, Optical resolution, Miscellaneous analytical procedures, The Z value as a measure of solvent polarity, Applications to biological systems, The relationship of complexes to reaction mechanism; Author index; Subject index.

Metallurgische Analysen: Chemische Untersuchung von technisch wichtigen Metallen und Erzen: József Mika. Akadémiai Kiadó (Publishing House of the Hungarian Academy of Sciences), 1964, S. 843, $12.00.

Erster Teil: Analyse der Metalle: 1. Eisen; 2. Aluminium und Aluminiumlegierungen; 3. Magnesium und Magnesiumlegierungen; 4. Kupfer un Kupferlegierungen; 5. Blei und Bleilegierungen; 6. Zinn und Zinnlegierungen; 7. Zink und Zinklegierungen; 8. Silber und Silberlegierungen.

Zweiter Teil: Analyse der Erze: 9. Eisen- und Manganerze; 10. Bauzit; 11. Magnesit und Dolomit; 12. Kupfer-, Blei- und Zinkerze.

Anhang: 1. Die gebräuchlichsten Lösungen; 2. Sonstige gebräuchliche Reagenzien; Empfohlene und verwendete Literatur; Sachregister.

New Methods of Analytical Chemistry: Ronald Belcher and Cecil L. Wilson in association with T. S. West. Chapman and Hall Ltd., London, Second Edition, 1964, 60s.

Contents: I. Titrimetric Standards: A. Conventional Acid-Base Standards: B. Recently Recommended Acid-Base Standards: C. Oxidation-Reduction Standards; II. Indicators: A. Acid-Base Indicators: (i) Chemiluminescent Indicators: (ii) Mixed Indicators: (iii) Miscellaneous Acid-Base Indicators: B. Redox Indicators: (i) Determination of Indicator Redox Potential: (ii) Phenathrolines and Bipyridyls: (iii) Diphenylamine Derivatives: (iv) Miscellaneous Redox Indicators: C. Metallochromic Indicators: (i) Calcium and Magnesium Indicators: (ii) Copper Selective Indicators: (iii) General Purpose Indicators: (iv) Metallofluorescent Indicators: (v) Screened Metallofluorescent Indicators: (vi) Chemiluminescent Complexometric Indicators: (vii) Extractive End-points: D. Miscellaneous Indicators: (i) Mercurimetric Indicators: (ii) Halide Titrations: (iii) Cyanide Titrations; III. Titrants; IV. Organic Reagents; V. Inorganic Reagents; VI. Selective Spectrophotometric Methods; VII. Precipitation from Homogeneous Solution: A. Change of pH: B. Direct Generation of Precipitating Agent: C. Precipitation by Removal of Solvent: D. Breakdown of Complexes; VIII. Solvent Extraction: A. General Considerations: (i) Ion-Association Complexes: (ii) Chelate Systems: B. Specific Applications: (i) 8-Hydroxyquinoline and Its Derivatives: (ii) Substituted Dithizones: (iii) Basic Dyestuffs: (vi) Monoximes and Dioximes: (v) 1,10-Phenanthroline and its Derivatives: (vi) Acetylacetone: (vii) Displacement Reagents: (viii) Miscellaneous Reagents; IX. Miscellaneous Methods. Subject Index: Author Index.

Principles and Methods of Chemical Analysis: HAROLD F. WALTON. Prentice-Hall, Inc., Englewood Cliffs, N.J., Second Edition, 1952, pp. 484.

1. Solubility of Precipitates: 2. Physical Form of Precipitates: 3. Impurities in Precipitates: 4. Precipitation from Homogeneous Solution: 5. Drying and Ignition of Precipitates: 6. Organic Precipitants and Extractants: 7. Complex Ions in Analytical Chemistry: 8. Ion Exchange in Analytical Chemistry: 9. Separations by Vaporisation: 10. Separations by Solvent Extraction: 11. Titrimetric Analysis: Introduction: 12. Oxidation-Reduction Potentials: 13. Methods of Potentiometric Titration: 14. Acid-Base Titrations: 15. Acid-Base Titrations in Non-aqueous Solvents: 16. Acid-Base Indicators: 17. Oxidation-Reduction Titrations: 18. Titrimetric Oxidation-Reduction Methods in Organic Chemistry: 19. Oxidation-Reduction Indicators: 20. Precipitation Titrations: 21. Complex-Forming Titrations: 22. Linear Titration Methods.

Thermal Methods of Analysis: WESLEY WM. WENDLANDT. John Wiley & Sons, Inc., New York, N.Y., 1964, pp. 424, $16.50.

I. General Introduction: II. Thermogravimetry: III. Automatic Recording Balances and Thermobalances: IV. Applications of Thermogravimetry: V. Differential Thermal Analysis: VI. Differential Thermal Analysis Instrumentation: VII. Applications of Differential Thermal Analysis: VIII. Thermometric Titrimetry: IX. Pyrolytic Techniques: X. Dynamic Reflectance Spectroscopy: XI. Thermal Analysis: XII. Miscellaneous Thermal Methods.

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following reviews published in Talanta are available from Journals Department, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"**Precipitation of Metal Chelates from Homogeneous Solution**" by F. H. Firsching.

"**Recent Developments in the Ring Oven Technique**" by H. Weisz.

"**Adsorption Indicators in Precipitation Titrations**" by R. C. Mehrotra and K. N. Tandon.

"**Radiometric Titrations**" by T. Braun and J. Tölgyessy.

"**Recent Uses of Liquid Ion Exchangers in Inorganic Analysis**" by H. Green.

New Pergamon Publications

Hard Metals Production Technology and Research in the U.S.S.R.

First publication of the scientific works of the All-Union Scientific Research Institute of Hard Metals.

Edited by S I Bashkirov

Articles dealing with production technology and the investigation of the structure and physical-mechanical properties of hard metals as well as X-ray, chemical and spectrographic analysis of hard metals and their raw materials.

Partial Contents:

Investigation of the wet grinding of hard alloy mixtures—V A Ivensen, N V Baranova, S S Loseva, I G Shatalova and O N Eiduk; Hard alloy cermets for drilling rock—G S Kreimer, O S Safonova and E M Bogino; Certain novel methods of treating hard alloy mixtures—I S Brokhin and D L Federmeyer; The removal of molybdenum from tungsten anhydride—Ye P Bogomil'skaya and R M Sviridovskaya; Tungsten-carbon hard alloy castings—Ye A Voronkova; Dynamic strength of WC–Co cermets at high temperatures—A I Baranov; Investigation of the carburizing process in tungsten carbide hard alloys with cobalt and nickel—I N Chaporova and Ye A Shchetlina; Investigation of solubility and phase composition in a silicon–carbon system—I S Brokhin and V F Funke; X-ray investigation of the heterogeneity of T15K6 hard alloy—A K Koval'skii and T G Makarenko; Determination of boron and chromium in chromium boride—V G Shcherbakov and R M Veitsman; Determination of small amounts of carbon in tungsten and molybdenum—V G Shcherbakov and Yu N Yurkevich.

364 pages, £7 ($20.00)

Methods in Polyphenol Chemistry

Proceedings of the Plant Phenolics Group Symposium held in Oxford.

Edited by J B Pridham, Lecturer in Organic Chemistry, Royal Holloway College, University of London

Well-known experts have contributed chapters covering the modern analytical techniques which are being used with polyphenolic compounds, including spectrophotometry, chromatography and electrophoresis. Special attention is paid to thin layer, polyamide and gas–liquid chromatography and N.M.R. spectroscopy, four of the latest techniques being used with polyphenols. The book will be of great value and interest to postgraduate students, university staff, Civil Service and industrial scientists in the fields of chemistry, biochemistry, botany, pharmacology and pharmacognosy.

Contents:

General Introduction—B R Brown; Ultraviolet spectroscopy of polyphenols—J B Harborne; Infrared spectroscopy of flavonoids—H Wagner; Nuclear magnetic resonance spectroscopy—R J Abraham; Spectrophotofluorimetry with particular reference to the fluorescence of phenols—J W Bridges; Paper chromatography of phenolics—E C Bate-Smith; Thin layer chromatography—V Thaller; Polyamide chromatography of flavonoids and anthraquinones—L Hörhammer; Specificity of inorganic oxy-acids in paper electrophoresis of carbohydrates and related compounds—H Weigel; Paper electrophoresis of phenolic compounds—J B Pridham; Gas–liquid chromatography—R O C Norman, J R Lindsay Smith and G K Radda; The quantitative analysis of phenolic compounds—T Swain and J L Goldstein.

156 pages, 50s ($7.50)

Offered for sale in the bookshops of

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