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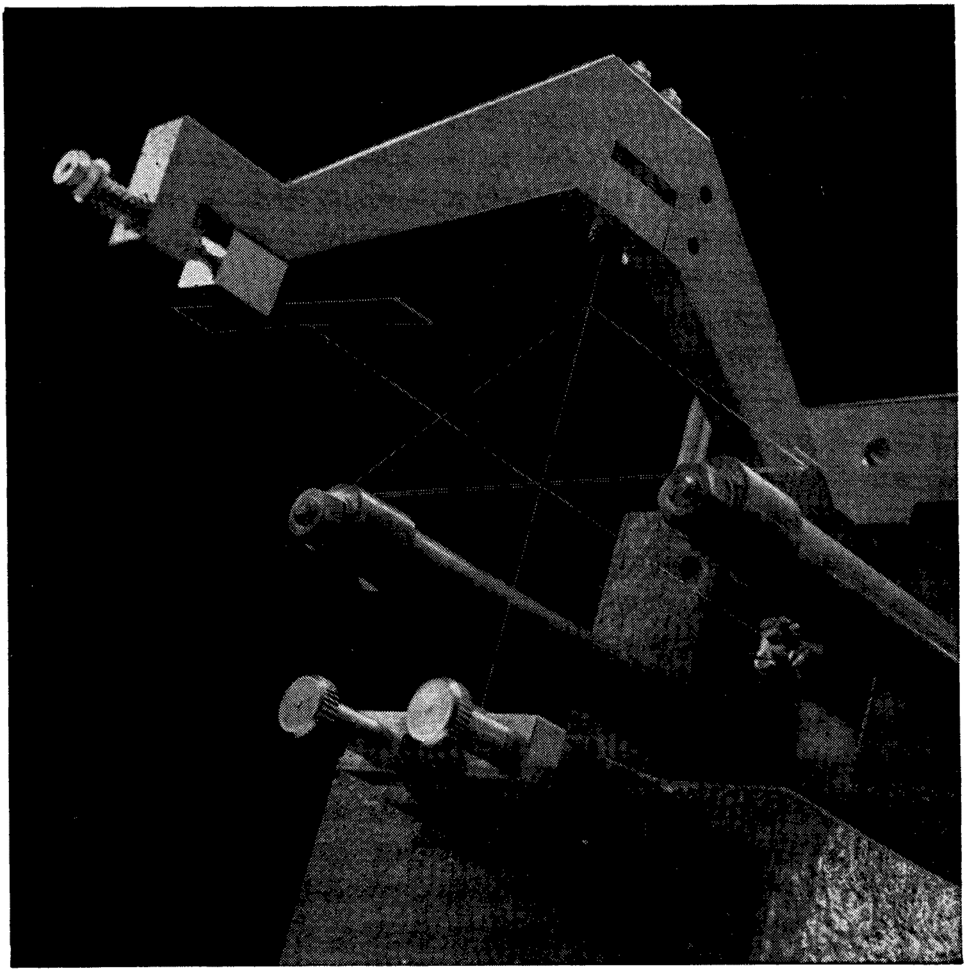

SUMMARIES FOR CARD INDEXES

Recent uses of liquid ion exchangers in inorganic analysis: H. GREEN, *Talanta*, 1964, **11**, 1561. (British Cast Iron Research Association, Bordesley Hall, Alvechurch, Birmingham, England.)

Summary—A review of recent uses of liquid ion exchangers in inorganic analysis is presented.

Determination of low concentrations of acetaldehyde in ethylene oxide: HERMAN HAGLUND, *Talanta*, 1964, **11**, 1581. (Research Laboratory, Mo och Domsjö AB, Örnsköldsvik, Sweden.)

Summary—The method is based on a qualitative test for acetaldehyde in which the reagents sodium nitroprusside and piperidine react with acetaldehyde to form a coloured substance that can be determined photometrically. This substance is unstable, however, and after reaching a maximum value in about 25 sec the absorbance decreases. Ethylene oxide also reacts with sodium nitroprusside to form brownish substances, but this reaction is slower, the colour not developing for 100–120 sec. If, therefore, the absorbance is measured about 25 sec after adding the reagents, any disturbance from the ethylene oxide is avoided.

Separation of bismuth from lead, copper and other elements by means of anion exchange: F. FEIK and J. KORKISCH, *Talanta*, 1964, **11**, 1585. (Analytical Institute, University of Vienna, IX, Währingerstrasse 38, Austria.)

Summary—The anion-exchange behaviour of bismuth and various other elements has been investigated in media consisting of methyl glycol and nitric acid. Through the determination of the distribution coefficients in such mixtures, a method for the anion-exchange separation of bismuth from many metal ions has been developed. A mixture of 90% methyl glycol and 10% $5M$ nitric acid is a suitable medium for this separation on the strongly-basic anion exchanger Dowex 1, X8. Only bismuth, thorium and lanthanum are strongly retained on the resin in these conditions. All other elements investigated, such as lead, copper, iron, *etc.*, are either only weakly adsorbed or are not absorbed. By means of this ion-exchange procedure, a series of analyses of copper-base alloys for bismuth has been carried out. The results show that this method can be used successfully for the quantitative isolation of bismuth from such materials. The final determination of bismuth in the eluates is performed by complexometric titration.

УСПЕХИ ЖИДКИХ ИОНО-ОБМЕННЫХ ВЕЩЕСТЬ В НЕОРГАНИЧЕСКОМ АНАЛИЗЕ:

H. Green, *Talanta*, **1964**, **11**, 1561.

Резюме—Приводится обзор новых применений жидких ионо-обменних веществ в неорганическом анализе.

ОПРЕДЕЛЕНИЕ НЕбОЛЬШИХ КОЛИЧЕСТЬ АЦЕТАЛЬДЕГИДА В ОКИСИ ЭТИЛЕНА:

Herman Haglund, *Talanta*, **1964**, **11**, 1581.

Резюме—Метод разработан из качественной пробы за ацетальдегид, помощью нитропруссида натрия и пиперидина. Образуется окрашенное вещество, поглощение которого достигает максимум в 25 сек., после чего снова уменьшается. Окис этилена тоже реагирует с нитропруссидом и творит коричневую окраску, но эта реакция медленее и максимум поглощения достигается только в 100–120 сек. Таким образом, если поглощение измеряется в 25 сек. после добавления реагентов, возможно избегнуть мешанию окиси этилена.

ОТДЕЛЕНИЕ ВИСМУТА ОТ СВИНЦА, МЕДИ И ДРУГИХ ЭЛЕМЕНТОВ ПОМОЩЬЮ ИОННОГО ОБМЕНА:

F. Feik and J. Korkisch, *Talanta*, **1964**, **11**, 1585.

Резюме—Исследовано поведение висмута и различных других элементов на ионообменных смолах в среде составленной от метилгликола и азотной кислоты. На основе определения коеффициентов распределения в таких смесах был разработан метод для отделения висмута од числа металл-ионов помощью ионного обмена. Самые лучшие разделения получены на сильно основной анионообменной смоле Дауекс I, X8 в смесе 90% метилгликола и 10% 5M азотной кислоты. В этих условиях на смоле задерживаются только висмут, торий и лантан; все остальные исследованные элементы как свинец, медь, железо и пр. проходят или только слабо адсорбируются. Пользуясь этим методом был проведен ряд определений висмута в медных сплавах. Результаты показывают что метод может применяться успешно для количественного выделения висмута из таких веществ. Определение висмута в элюатах проведено методом комплексометрического титрования.

Nucleation of lead chromate from homogeneous solution: NORTON HABERMAN and LOUIS GORDON, *Talanta*, 1964, **11**, 1591. (Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio, U.S.A.)

Summary—On the basis of the Christiansen-Nielsen model for nucleation, the nucleus of lead chromate precipitated from homogeneous solution has been found to consist of about five ions. The critical supersaturation values of solutions of lead chromate are dependent upon the method of filtration; however, a change in supersaturation of about 25% is without effect on the size of the critical nucleus.

Separation and determination of tantalum and niobium by precipitation from homogeneous solution: R. DAMS and J. HOSTE, *Talanta*, 1964, **11**, 1599. (Laboratory of Analytical Chemistry, Ghent University, Belgium.)

Summary—An attempt to separate niobium and tantalum by precipitation from homogeneous solution by thermal decomposition of their peroxy complexes, in the presence of tannin and oxalate, has been only moderately successful. A more satisfactory separation of tantalum and niobium for ratios from 50:1 to 1:30 is obtained by extracting the bisulphate melt with ammonium oxalate before adding hydrogen peroxide, hydrochloric acid and tannin. For a tantalum/niobium ratio of 1:1 the niobium coprecipitation is reduced to 5%. Furthermore, two alternative possibilities are presented: (1) a quantitative recovery of a tantalum precipitate at small oxalate and high tannin concentration, leaving 90% of the tantalum-free niobium in solution; (2) an 85% recovery of niobium-free tantalum at high oxalate and small tannin concentration. A study of the coprecipitation process of niobium shows that the distribution coefficients follow a logarithmic pattern, true homogeneous mixed crystals being formed.

Gravimetric analysis of tantalocolumbites by precipitation from homogeneous solution: R. DAMS and J. HOSTE, *Talanta*, 1964, **11**, 1605 (Laboratory of Analytical Chemistry, Ghent University, Belgium.)

Summary—An analysis of complex tantalocolumbites has been carried out by precipitation from homogeneous solutions. A homogeneous precipitation of tungsten, titanium, tantalum and niobium by thermal decomposition of the soluble peroxytungstates, described in previous papers, is used. Corrections for incomplete precipitation and coprecipitation phenomena are applied on the basis of the experimentally found values. Silicon and tin are separated by volatilisation as fluoride and iodide, respectively. Iron is extracted by means of isopropyl ether and the rare earth metals are precipitated homogeneously from an oxalate solution. Manganese is precipitated as the ammonium phosphate. The results are in good agreement with an independent method, the standard deviations being within 1% for the major constituents.

ОБРАЗОВАНИЕ ЦЕНТРОВ КРИСТАЛЛИЗАЦИИ ХРОМАТА СВИНЦА ИЗ ГОМОГЕННОГО РАСТВОРА:

Norton Haberman and Louis Gordon, *Talanta*, 1964, **11**, 1591.

Резюме—На основе модели Христиансен—Нильсен для образования центров кристаллизации авторы пришли до вывода что зародыш кристалла состоится из около 5 ионов. Критическое пересыщение растворов хромата свинца зависимо от метода фильтрации; между тем, перемена пересыщения от 25% не имела действие на величину критического ядра.

ВЫДЕЛЕНИЕ И ОПРЕДЕЛЕНИЕ ТАНТАЛА И НИОБИЯ ОСАЖДЕНИЕМ ИЗ ГОМОГЕННОГО РАСТВОРА:

R. Dams and J. Hoste, *Talanta*, 1964, **11**, 1599.

Резюме—Попытка выделять ниобий и тантал путем гомогенного осаждения в присутствии таннина и оксалата и теплового разложения комплексов перекиси не совсем удовлетворила. Между тем лучшие результаты для отношения тантала и ниобия 50 : 1 до 1 : 30 получились экстрагированием бисульфатовой плави оксалатом аммония перед добавлением H_2O_2, HCl и таннина. При отношении тантал: ниобий 1 : 1 совместное осаждение ниобия уменьшается до 5%. Предлагаются две возможности: (1) количественное выделение осадка тантала при низкой концентрации оксалата и высокой концентрации таннина, оставляя 90% свободного од тантала ниобия в растворе; (2) выделение 85% свободного од ниобия тантала при високой концентрации оксалата и низкой концентрации таннина. Изучение соосаждения ниобия показало, что коэффициент распределения следит логарифмическое течение, при образовании гомогенных смешанных кристаллов.

ВЕСОВОЙ АНАЛИЗ ТАНТАЛОНИОБИТОВ ПУТЕМ ОСАЖДЕНИЯ ИЗ ГОМОГЕННОГО РАСТВОРА:

R. Dams and J. Hoste, *Talanta*, 1964, **11**, 1605.

Резюме—Проведен анализ сложных танталониобитов методом осаждения из гомогенных растворов. Применилось гомогенное осаждение вольфрама, титана, тантала и ниобия путем теплового разложения растворимых пероксивольфраматов, которое было описано в прежних статьях. Коррекции для неполного осаждения и совместного осаждения вычислены на основе экспериментальных данных. Кремний и олово выделены в форме фторида и иодида. Железо экстрагируется изопропиловым эфиром, а редкоземельные элементы гомогенно осаждаются из раствора оксалата. Марганец осаждается в форме фосфата аммония. Результаты хорошо соглашаются с независимым методом, стандартные отклонения меньше чем 1% для главных компонентов.

Contributions to the basic problems of complexometry—XVII: Determination of zinc and cadmium in the presence of each other: Rudolf Přibil and Vladimír Veselý, *Talanta*, 1964, **11**, 1613. (Analytical Laboratory, Polarographic Institute of J. Heyroský, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—A new method for separating cadmium from zinc by precipitation as $Cd(phen)_2I_2$ is reported. Even very small amounts of zinc can be determined complexometrically in highly ammoniacal media by back-titration of an added excess of DCTA with calcium(II) using Methylthymol Blue as indicator.

The determination of acetone in butanone-2 by phase separation: D. W. Rogers, *Talanta*, 1964, **11**, 1617. (Chemistry Department, Long Island University, Brooklyn 1, New York, U.S.A.)

Summary—Binary solutions of acetone in butanone-2 have been analysed by adding a constant amount of water and determining the temperature at which phase separation takes place. Because butanone-2 and water have a lower critical solution temperature, solutions are clear at lower temperatures and opalescent at higher temperatures. The weight percent of acetone in the original binary solution of ketones is a function of the phase-separation temperature, enabling the analyst to construct a calibration curve and determine unknown solutions directly. The error is about 0·1 absolute %.

Anion-exchange separation of beryllium, vanadium and other elements from large amounts of uranium: J. Korkisch and S. S. Ahluwalia, *Talanta*, 1964, **11**, 1623. (Analytical Institute of the University of Vienna, IX, Währingerstrasse 38, Austria.)

Summary—A method is described for the anion-exchange separation of small quantities of beryllium, vanadium, magnesium, calcium, aluminium, gallium and indium from gram-amounts of uranium. For this purpose, a medium consisting of 95% methanol and 5% $5M$ nitric acid is passed through a resin bed of Dowex 1, X8. By subsequent washing of the resin with a methanol-nitric acid mixture of the same composition, these metal ions are preferentially eluted from the column, whereas uranium is still retained by the anion exchanger. In the eluates the elements are determined by means of spectrophotometric or titrimetric procedures.

ВКЛАД К ОСНОВНЫМ ПРОБЛЕМАМ КОМПЛЕКСОМЕТРИИ XVII. ОПРЕДЕЛЕНИЕ ЦИНКА И КАДМИЯ ОДНОГО В ПРИСУТСТВИИ ДРУГОГО

RUDOLF PRIBIL and VLADIMIR VESELY, *Talanta*, 1964, **11**, 1613.

Резюме—Описывается новый метод для отделения кадмия от цинка осаждением в форме фенантролин-иодида $Cd/Phen/_2J_2$. Тоже определяются небольшие количества цинка комплексометрическим методом в сильно аммиачной среде путем обратного титрования солью кальция. Метилтимол голубая служит как индикатор.

ОПРЕДЕЛЕНИЕ АЦЕТОНА В БУТАНОНЕ-2 МЕТОДОМ ФАЗОВОГО РАЗДЕЛЕНИЯ:

D. W. ROGERS, *Talanta*, 1964, **11**, 1617.

Резюме—Бинарные растворы ацетоне в бутаноне-2 были анализированы добавлением константного количества воды и определением температуры при которой является разделение фаз. Бутанон-2 и вода имеют нижнюю критическую температуру растворения, потому растворы ясны при нижних температурах, а опалесцируют при высших температурах. Весовой процент ацетона в исходной бинарной смесе кетонов является функцией температуры, при которой происходит разделение фаз; на основании этих данных возможно устроить стандартную кривую и анализировать растворы незнакомого состава. Абсолютная ошибка около 0.1%.

ОТДЕЛЕНИЕ БЕРИЛЛИЯ, ВАНАДИЯ И ДРУГИХ ЗЛЕМЕНТОВ ОТ БОЛЬШИХ КОЛИЧЕСТЬ УРАНА МЕТОДОМ АНИОННОГО ОБМЕНА:

J. KORKISCH and S. S. AHLUWALIA, *Talanta*, 1964, **11**, 1623.

Резюме—Описывается метод для отделения небольших количеств бериллия, ванадия, магния, кальция, алюминия, галлия и индия от граммовых количеств урана методом анионного обмена. Это получается пропусканием смеси от 95% метилового спирта и 5% 5N азотной кислоты через слой смолы Дауеск 1, X8. Элюированием смолы смесью метиловый спирт-азотная кислота тогоже состава отделяются упомянутые металл-ионы, междутем как уран задерживается на смоле. В элюатах элементи определяются спектрофотометрическим или титриметрическим методами.

A selective extraction system for trace amounts of silver: R. M. Dagnall and T. S. West, *Talanta*, 1964, **11**, 1627. (Department of Chemistry, Imperial College, London S.W.7, England.)

Summary—Silver can be extracted from near-neutral aqueous solution into nitrobenzene as the ion-association system formed between its 1,10-phenanthroline complex and bromopyrogallol red. In the presence of EDTA, mercury(II) and bromide ions as masking agents, the extraction system is highly selective. Of 42 ions examined, only thiosulphate and large amounts of gold interfere. The colour system is very sensitive ($\epsilon = 32{,}000$). Also, it can readily be applied to the indirect determination of concentrations of cyanide down to 0·026 ppm by determination of an added excess of silver.

Determination of beryllium by means of hexamminecobalt(III) carbonatoberyllate—I: Composition of the precipitate and its suitability as a weighing form for beryllium: R. G. Monk and K. A. Exelby, *Talanta*, 1964, **11**, 1633. (Atomic Weapons Research Establishment, U.K.A.E.A., Aldermaston, Berks, England.)

Summary—The precipitate obtained when hexamminecobalt(III) chloride is added to a solution of beryllium in excess ammonium carbonate has been analysed and its behaviour under different humidity conditions examined. The composition is that of hexamminecobalt(III) hexacarbonato-oxo-tetraberyllate $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot xH_2O$, as suggested by Sen Gupta, rather than that of Pirtea $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$. x depends on the humidity of conditioning, varying between 10·8 and 11·1 at relative humidities between 32 and 80%. Drying the precipitate *in vacuo* over anhydrous magnesium perchlorate or phosphorus pentoxide results in 3 molecules of water being retained. The compound as normally precipitated may be a mixture of the deca- and dodecahydrates that Sen Gupta prepared. After conditioning at a definite humidity and if an empirical factor is used, the precipitate may be suitable as a gravimetric form for determining beryllium where precision requirements are not too exacting.

Precipitation of copper 8-hydroxyquinaldate from homogeneous solution: R. P. Graham, E. J. Billo and J. A. Thomson, *Talanta*, 1964, **11**, 1641. (Burke Chemical Laboratories, McMaster University, Hamilton, Ontario, Canada.)

Summary—Copper can be precipitated quantitatively, over a wide range of pH, by 8-hydroxyquinaldine produced from the hydrolysis of 8-acetoxyquinaldine. The copper 8-hydroxyquinaldate can be weighed as either the monohydrate or the anhydrous dichelate. Differences in the appropriate pH conditions, between the PFHS and conventional precipitation methods, and between thorium and copper precipitations from homogeneous solution, are accounted for.

ИЗБИРАТЕЛЬНОЕ ЭКСТРАГИРОВАНИЕ СЛЕДОВ СЕРЕБРА:

R. M. Dagnall and T. S. West, *Talanta*, **1964, 11,** 1627.

Резюме—Серебро может экстрагироваться из почти нейтрального раствора в нитробензол в форме ионной ассоциации между его комплексом с 1,10-фенантролином и бромпирогаллол красным. В присутствии ЭДТА, ртути(II) и бромид-ионов как маскирующих агентов эта система экстракции является високо избирательной. Между исследованными 42 ионами только тиосульфат и большие количества золота мешают экстракции. Окраска очень чувствительна ($E = 32{,}000$). Метод успешно применяется для косвенного определения цианид-ионов до концентрации 0,026 мг/л, определяя избиток добавленного серебра.

ОПРЕДЕЛЕНИЕ БЕРИЛЛИЯ В ФОРМЕ ГЕКСАММИНОКОБАЛЬТ(III)-КАРБОНАТОБЕРИЛЛАТА. I—СОСТАВ ОСАДКА И ЕГО ПРИМЕНЕНИЕ ДЛЯ ВЕСОВОГО ОПРЕДЕЛЕНИЯ БЕРИЛЛИЯ:

R. G. Monk and K. A. Exelby, *Talanta*, **1964, 11,** 1633.

Резюме—Исследован осадок получен добавлением хлористого гексамминокобальта(III) в раствор бериллия в избитке карбоната аммония и изучено его поведение при различных условиях влажности. Состав осадка соответствует формуле кобальт(III)-гексакарбонат-оксо-тетрабериллат $[Co(NH_3)_6]_2[Be_4O(CO_3)_6] . xH_2O$ как предложено Сен Гуптом, лучше чем формуле Пиртее: $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3] . 3H_2O$. X зависит от влажности и колебает между 10,8 и 11,1 при относительной влажности между 32 и 80%. После высушивания во вакууме над безводным перхлоратом магния или фосфорным ангидридом сохраняются 3 молекулы воды. Осадок получен нормальным осаждением может представлять собой смесь дека- и додекагидратов, приготовленных Сен Гуптом. После кондиционирования при определенной влажности и применением эмпирического фактора, осадком можно пользоваться для весового определения бериллия если не изискуется большая точность.

ОСАЖДЕНИЕ 8-ГИДРОКСИХИНАЛДАТА МЕДИ ИЗ ГОМОГЕННОГ РАСТВОРА:

R. P. Graham, E. J. Billo and J. A. Thomson, *Talanta*, 1964, **11,** 1641.

Резюме—Медь осаждается количественно в широкой области pH 8-гидроксихиналдином образованным помощью гидролиза 8-ацетоксихиналдина. 8-гидроксихиналдат меди можно взвешивать в форме моногидрата или безводного двойного внутреннего комплекса. Приняты во внимание разницы в условиях pH между PFHS и обыкновенными методами осаждения и между осаждением тория и меди из гомогенного раствора.

Spectrophotometric investigation of the nature and stability of silver(II) in acidic sulphate media: G. A. RECHNITZ and S. B. ZAMOCHNICK, *Talanta*, 1964, **11**, 1645. (Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.)

Summary—A spectrophotometric study of silver(II) in sulphuric acid solution indicates the formation of two sulphato complexes, in the range 4–18*M* H_2SO_4, with absorbance peak maxima at 361 and 260 mμ, respectively. In 15*M* H_2SO_4 the molar absorptivity of silver(II) is $3{\cdot}11 \times 10^4$ at 361 mμ. Kinetic studies of the reduction of silver(II) by the solvent suggest a rate-determining step first order in silver(II) and yield a pseudo first-order rate constant of $1{\cdot}9 \times 10^{-1}$ min^{-1}. Further studies as a function of H_2SO_4 concentration show that the specific decomposition rate of the two complexes is identical and that changes in H_2SO_4 concentration only serve to shift the concentration equilibrium between the two complexes.

Photometric titrations—X: The EDTA titration of iron(III) in the presence of high concentrations of bismuth: H. FLASCHKA and J. GARRETT, *Talanta*, 1964, **11**, 1651. (School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia, U.S.A.

Summary—In solutions containing a high concentration of ammonium chloride, bismuth is masked as the chloro complex, and iron(III) can be titrated with EDTA to a photometric end-point using sulphosalicylic acid as the indicator. Up to a mole ratio Bi:Fe of about 2,000, good results are obtained. At higher ratios slightly high results are obtained for the iron. The influence of some other metal ions on the titration has been studied.

Some antipyrine derivatives in the analytical chemistry of the platinum metals: A. I. BUSEV and V. K. AKIMOV, *Talanta*, 1964, **11**, 1657. (Department of Chemistry, M. V. Lomonosov State University, Moscow, U.S.S.R.)

Summary—The reaction of quadrivalent osmium and iridium with antipyrine and some of its derivatives has been studied, and it has been shown that in acidic solutions the compounds $(R.H)_2MeX_6$ are formed. The extraction of the halide complexes of osmium, iridium, ruthenium, rhodium, platinum and palladium with diantipyrylpropylmethane by dichloroethane has been investigated. An extraction–photometric method is proposed for determining 2–20 μg/ml of osmium in the presence of 40 mg of ruthenium and for determining 4–40 μg/ml of iridium in the presence of 4 mg of rhodium. The error of the determination is ±10%. A gravimetric method is proposed for determining 5–13 mg of osmium and iridium with diantipyrylpropylmethane and diantipyrylmethane. The error of the determination is ±3%. The possibility is shown of the extractive separation of small amounts of iridium and rhodium, platinum and rhodium, and palladium and rhodium, using diantipyrylpropylmethane.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ ХАРАКТЕРА И УСТОЙЧИВОСТИ СЕРЕБРА(II) В КИСЛЫХ СУЛЬФАТНЫХ СРЕДАХ:

Garry A. Rechnitz and S. B. Zamochnick, *Talanta*, 1964, **11**, 1645.

Резюме—Спектрофотометрическое исследование серебра(II) в сернокислом растворе указивает на образование двух сульфатных комплексов в области 4–18M H_2SO_4, имеющие максимум поглощения при 361 и 260 ммк, соответственно. В 15M H_2SO_4 молярная поглотительность серебра(II) равна $3{,}11 \times 10^4$ при 361 ммк. Кинетическое исследование восстановлкния серебра(II) растворительем указивает на реакцию первого порядка, определяющую общую скорость реакции; константа псевдо-первого порядка равна $1{,}9 \times 10^{-1}$ мин$^{-1}$. Дальнейшие исследования эффекта концентрации H_2SO_4 показивают что удельные скорости разложения этих двух комплексов одинаковы и что изменением концентрации H_2SO_4 только перемещается равновесие между комплексами.

ОПРЕДЕЛЕНИЕ ЖЕЛЕЗА (III) ТИТРОВАНИЕМ С ЭДТА В ПРИСУТСТВИИ БОЛЬШИХ КОЛИЧЕСТЬВ ВИСМУТА:

H. Flaschka and J. Garrett, *Talanta*, 1964, **11**, 1651.

Резюме—В растворах содержающих большие количества хлорида аммония висмут маскируется в форме хлоро-комплекса и железо(III) удается определить титрованием с ЭДТА до фотометрического конца, пользуясь сульфосалициловой кислотой как индикатором. Все до мольного отношения Bi/Fe около 2000 получаются хорошие результаты. При высших концентрациях висмута результаты дла железа незначительно повышены. Изучено влияние некоторых других ионов металла на титрование.

ПРИМЕНЕНИЕ НЕКОТОРЫХ ПРОИЗВОДНЫХ АНТИПИРИНА В АНАЛИТИЧЕСКОЙ ХИМИИ ПЛАТИНОВЫХ МЕТАЛЛОВ:

A. I. Busev and V. K. Akimov, *Talanta*, 1964, **11**, 1657.

Резюме—Изучено взаимодействие четырехвалентного осмия и иридия с антипирином и некоторыми его производными и показано, что в кислых растворах образуются ониевые соединения $(R{\cdot}H)_2MeX_6$. Исследованы процессы экстракции галогенидных комплексов осмия, иридия, рутения, родия, платины и палладия с диантипирилпропилметаном дихлорэтаном. Предложен экстракционно-фотометрический метод определения 2–20 мкг/мл осмия в присутствии 40 мг рутения и 4–40 мкг/мл иридия в присутствии 4 мг родия с помощью диантипирилпропилметана. Погрешность определения ±10%. Предложен гравиметрический метод определения 5–13МГ осмия и иридия с помощью диантипирилпропилметана и диантипирилметана. Потрешность определения ±3% Показана возможность экстракционного разделения малых количеств иридия и родия, платины и родия, палладия и родия с помощью диантипирилпропилметана.

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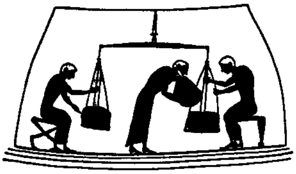

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, Vol. 3. Pergamon Press, London, 2nd Ed., 1956, p. 214.
[3] A. B. Smith, *The Effect of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

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TALANTA REVIEW*

RECENT USES OF LIQUID ION EXCHANGERS IN INORGANIC ANALYSIS

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Birmingham, England

(*Received* 27 *June* 1964. *Accepted* 20 *August* 1964)

Summary—A review of recent uses of liquid ion exchangers in inorganic analysis is presented.

INTRODUCTION

Separations using liquid ion exchange may be said to date from the publication, in 1948, of a paper by Smith and Page[1] entitled "The Acid-Binding Properties of Long-Chain Aliphatic Amines". Since then, increasing interest has been shown in the use, as extractants, of those high molecular weight acids and bases which possess low solubility in water and high solubility in water-immiscible solvents.

The operation of liquid ion exchangers involves selective transfer of solute between two immiscible phases, an aqueous phase and an organic phase containing the liquid exchanger. The technique for liquid ion exchange separation is, therefore, identical to that employed in general solvent extraction separations. From the very first, liquid ion exchange has been compared with resinous ion-exchange because the behaviour of analogous functional groups in the two systems is frequently similar. From this similarity, by reference to available data on extractions with ion-exchange resins, it is possible to make a reasonable prediction of the likely course of the corresponding liquid ion-exchange extractions. Liquid ion exchangers may be employed in a similar manner to resinous exchangers except that, although the course of the reaction may involve 'salt-splitting', the ultimate products will not be acids or bases, as may be obtained with solid resins. They may be employed for the extraction of acids and bases, when the extraction from aqueous solution is by a neutralisation process to form a salt which is soluble in the organic solvent but insoluble in water, *e.g.*, $RNH + HX \rightarrow RNH_2X$. Alternatively, the same liquid exchangers may be used in the salt form when ions may be exchanged with those in the aqueous solution, *e.g.*, $RNH_2Cl + NaNO_3 \rightleftharpoons RNH_2NO_3 + NaCl$. This is, of course, a reversible reaction and when the organic phase contains the amine chloride a strong solution of sodium nitrate will strip the amine of chloride ions, while if amine nitrate in the organic phase is treated with a strong solution of sodium chloride the amine is stripped of nitrate ions. Regeneration of the appropriate amine salt is accomplished in these cases, and if the amine salt is treated with an alkaline solution, such as aqueous ammonia, sodium hydroxide or sodium carbonate, the free amine is obtained. Similar considerations apply in the case of cation exchangers, where regeneration can be achieved using suitable acid solutions. Selectivity is obtained when using liquid ion-exchangers by the usual means—control of pH and salt concentration, adjustment of valency, addition of complexing agents and probably most important of all choice of organic diluent.

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It will be seen that liquid ion exchangers combine many of the advantages of both solvent extraction and ion exchange. There are, however, a number of difficulties and disadvantages associated with their use, and an appreciation of these is essential if the full advantage of the combination of solvent extraction and ion exchange is to be obtained. The major difficulty is associated with the formation of emulsions between the organic and aqueous phases, making separation difficult and on some occasions impossible. The relative viscosities and densities of the two phases are of major importance here and, because liquid exchangers usually possess some surface activity, it is necessary to select those having a low activity and to use those conditions which will minimise the formation of stable emulsions. Such conditions are control of temperature, choice of acid and amount of free acid in the aqueous phase, organic diluent for the exchanger, relative volumes of organic and aqueous phases and concentration of the exchanger in the organic phase; the addition of 2–3% of a higher alcohol to the organic phase has proved effective in preventing emulsion formation in some cases.

The expense associated with the use of organic liquids for solvent extractions is not usually of major importance in laboratory applications, but organic solvents can be dangerous if care is not taken in handling and storage, and the exchangers themselves may constitute a certain hazard. For example, in the case of the aliphatic amines used as anion exchangers, the manufacturers point out that although the volatility is low, it is very important, particularly before dilution, to provide adequate ventilation to prevent inhalation of the vapours. Every precaution should be taken to avoid contact with the eyes or prolonged contact with the skin.

It is advisable to keep apparatus used for liquid ion-exchange extractions separate from that used for normal solvent extraction because separating funnels, in particular, are difficult to render completely free from the exchangers. If this is not possible, treatment with a solution containing 5 g of ammonium fluoride and 5 ml of hydrochloric acid in 100 ml of water followed by 10% sodium carbonate solution is usually an effective method of cleaning the glassware.

Another disadvantage in the use of liquid ion exchangers is the fact that, unlike many of the common solvent extraction separations, it is usually necessary to back-extract the required species from the organic phase to complete the determination. It is sometimes possible to use the organic phase directly for determination of the extracted ion or ions, *e.g.*, by aspirating directly into a flame and measuring by means of flame photometry or atomic absorption spectroscopy;[17] by employing a cellulose column impregnated with the liquid exchanger,[2] when metal ions may be recovered on ashing the cellulose and exchanger. If radioactive materials are under investigation, direct measurement of the activity present in the organic phase is possible. Back-extraction procedures can be very tedious where successive extractions are involved, because the organic layer is usually chosen to be the lower layer, when the extraction is being made, for ease of separation; if this layer has to be back-extracted manipulation is much more difficult. Before liquid ion exchange becomes as popular a method of separation as solvent extraction procedures have become, it will be necessary for simple techniques to be devised which utilise the organic phase directly. This is one of the great assets when employing normal solvent extraction methods.

Compared with resinous ion exchange the use of liquid ion exchangers offers a much more rapid method of separation of the required ionic species. In its normal method of use a liquid exchanger is closely similar to a solid resinous exchanger used in the 'batch analysis' technique. It does not, as yet, offer the same range of potential separations. For example, it is not possible to employ the technique of 'frontal analysis' in the same way as with solid resins except by the use of cellulose columns impregnated with the liquid exchanger referred to earlier. This does make possible the use of selected elution and it is claimed that the elution peaks are very narrow, but the preparation of the column appears to be a much longer process than the preparation of resin columns and the advantages accruing are rather marginal.

A comprehensive list of liquid ion exchangers has been given by Coleman, Blake and Brown,[3] but many of those listed have not been extensively used in analysis, and the exchangers mentioned here are those which have become generally accepted as the major materials for carrying out liquid ion exchange. Attention is also directed to a paper by Kunin and Winger.[4] Because of these authors' association with the Rohm and Haas Company, who manufacture Amberlite ion-exchange materials, the information given is invaluable as an introduction to the use of liquid ion-exchange materials.

Much of the earlier work up to 1960, covering extraction with liquid anion exchangers, has been reported by Moore.[5] The section in the present review dealing with liquid anion-exchangers is intended to cover the more important published work since then, with particular reference to the analysis of the more commonly encountered inorganic materials.

In order to prevent this review from becoming excessive in length, work carried out on the transuranic elements has not been included. Papers presented at the 1962 Conference on Solvent Extraction at Gatlinburg, U.S.A., many of which are now in the open literature,[6] effectively review the position regarding these elements.

LIQUID ANION EXCHANGERS

Liquid anion exchangers, at present available, are based on primary, secondary and tertiary aliphatic amines. They are of high molecular weight, water insoluble but soluble in many organic solvents, such as petroleum distillates, aliphatic and aromatic hydrocarbons, high molecular weight alcohols and chlorinated hydrocarbons. For laboratory separations only a small number of the amines which are commercially available have so far been examined and recommended for particular applications and of these the Amberlite exchangers have received by far the greatest attention. The important relevant properties of Amberlite LA.1 [*N*-dodecenyl(trialkylmethyl)amine] and Amberlite LA.2 [*N*-lauryl(trialkylmethyl)amine], both secondary amines, are summarised in Table I.

TABLE I.—SUMMARY OF RELEVANT PROPERTIES OF AMBERLITE EXCHANGERS LA.1 AND LA.2

Property	Amberlite LA.1	Amberlite LA.2
Molecular weight	351–393	353–395
Neutral equivalent	380–410	360–380
Acid binding capacity,		
mequiv/g	2·5–2·7	2·6–2·8
mequiv/ml	2·1–2·3	2·2–2·3
Density (25°), *g/ml*	0·84	0·83
Viscosity (25°), *cp*	72	18
Flash point, °*C*	*ca.* 105°	*ca.* 180°

These exchangers are usually employed at solution strengths varying from 2 to 20% in an inert organic solvent and, as may be expected, the capacity for ion exchange of a particular exchanger, for the same anion, is directly proportional to its concentration in the organic phase. Figures given by the manufacturers for Amberlite LA.1 show that, using kerosene as diluent, 1 litre of 0·05*M* amine has a capacity for $U_3O_8^{2-}$ ions of 1·78 g, while a 0·1*M* solution of amine has a capacity of 3·56 g and a 0·25*M* solution a capacity of 8·88 g/litre. A difference in capacity for ion exchange is exhibited for different ions. Table II shows how this capacity varies with the anion in question for Amberlite LA.1 and LA.2 when 0·1*M* solutions of the exchanger in kerosene are equilibrated with an equal volume of 0·1*M* acid in water. These extraction figures can be improved upon by the addition of a salt, such as sodium chloride, nitrate, sulphate, acetate or tartrate as appropriate, to increase the anion concentration.

TABLE II.—EXTRACTION OF ANIONS[a] BY AMBERLITE LA.1 AND LA.2

Acid	Extraction, %	
	Amberlite LA.1	Amberlite LA.2
Hydrochloric	77·3	88·6
Nitric	85·3	94·4
Sulphuric	74·5	88·0
Acetic	2·7	8·9
Tartaric	1	44

[a] In the form of the free acid.

Several metals form anionic complexes in solutions of mineral acids and it is possible to extract many of these complexes using anion exchangers. Such metals include niobium, tantalum, chromium, zirconium, zinc, uranium, titanium, vanadium and tin, while the anionic complexes may contain radicals such as sulphate, nitrate, oxalate, chloride or fluoride. Figure 1 shows the effect of variation in free sulphuric acid

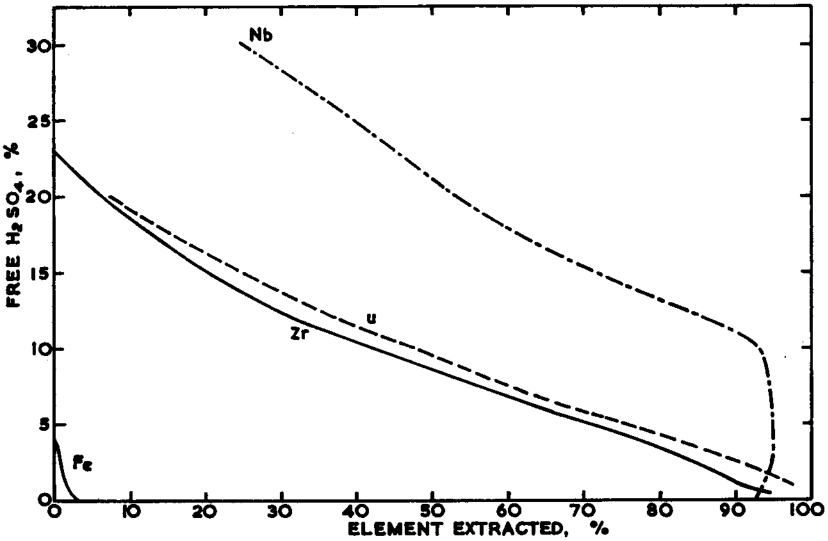

FIG. 1.—Typical curves for liquid ion-exchange extractions.
(Extractions made from sulphuric acid media using a 2:1 ratio of aqueous/organic phases and 4% of Amberlite LA.1 in chloroform[7,8,9].)

content of solution on degree of extraction of some metals as anionic sulphate complexes. Each extraction was made from a 100-ml volume of solution containing 0·02 g of the element and sulphuric acid only, except in the case of niobium when 0·1 g of oxalic acid was also present to prevent hydrolysis and precipitation of the hydrated pentoxide. Only one extraction was made in each case using 50 ml of 4% Amberlite LA.1 in chloroform. Iron(III) is seen to extract only slightly using sulphuric acid media and even then only at very low free acid contents. Zirconium and uranium give very similar extractions to one another, the degree of extraction increasing as the acid concentration decreases. Two extractions with 50-ml volumes of the exchanger at the 1–2% of free sulphuric acid level will then give virtually 100% extraction of both metals. Niobium extraction is appreciable even at the 30% of free sulphuric acid concentration, and from a 5% acid solution two extractions again give a virtual 100% removal.

Under similar conditions, Green[8] has shown that titanium and vanadium do not extract from sulphuric acid solutions alone using Amberlite LA.1. In fact, at the lower sulphuric acid concentrations titanium is hydrolysed. If sufficient fluoride ion is added to the solution of titanium containing 5% of free sulphuric acid to convert the titanium sulphate to titanium fluoride, then 95% of the titanium may be extracted with one 50-ml volume of the exchanger and virtually 100% using two 50-ml volumes. Vanadium gives only a partial and variable extraction in the presence of fluoride. When hydrogen peroxide is used in conjunction with the 5% sulphuric acid solution, 65–70% of the titanium is extracted with one 50-ml volume and 90–95% with two volumes of exchanger. Vanadium extraction is about 30% with one 50-ml volume of exchanger and about 50% with two volumes.

Conditions for the extraction of a number of metal ions from hydrochloric acid solutions, using a 10% solution of Amberlite LA.1 in xylene, have been investigated by Nakagawa.[10,11] A summary of his results is given in Table III. The range of

TABLE III.—EXTRACTIONS USING 10% AMBERLITE LA.1 IN XYLENE

Element	Optimum HCl range, *M*	Extent of extraction,[a] %
Cadmium(II)	2–6	95
Chromium(VI)	1–6	Almost quantitative[b]
Chromium(III)	—	Negligible
Copper(II)	7	35
Gallium(III)	>4	Quantitative
Germanium(IV)	8–11	Almost quantitative
Indium(III)	7	86
Iron(III)	6	Quantitative
Lead(II)	1·5	40
Manganese(II)	1–10	<12
Mercury(II)	1–8	Quantitative
Selenium(IV)	>9	Almost quantitative
Tellurium(IV)	4–6	Quantitative
Tin(IV)	5–6	Almost quantitative
Titanium(IV)	—	No extraction
Vanadium(V)	6–8	90[b]
Vanadium(IV)	—	No extraction

[a] One extraction.

[b] Reduction of V^{5+} to V^{4+} and of Cr^{6+} to Cr^{3+} occurs in solutions more than 6*M* in HCl.

hydrochloric acid concentration given in the table for each element is that over which maximum extraction occurs; outside this optimum range, extraction for any particular element may still be appreciable. Cadmium can be extracted from hydrochloric acid solutions as low as 0·1*M*, with maximum extraction at 2–6*M* and decreasing extraction with increased acid concentration to become 23% in concentrated acid. Tervalent chromium shows negligible extraction but sexivalent chromium gives almost quantitative extraction from solutions 1–6*M* in hydrochloric acid. More concentrated acid tends to reduce the chromium and lower the amount extracted. Back-extraction of the chromium from the organic phase only required that the aqueous phase contained a reducing agent, such as iron(II) sulphate or hydroxylamine hydrochloride.

Copper extracts from hydrochloric acid solutions greater than 3*M* with a maximum extraction of 35% from 7*M* acid. Extraction of germanium commences from 4*M* acid, becoming almost quantitative between 8 and 11*M*. The extraction of indium increases from 12% in 1*M* hydrochloric acid to 86% in 7*M*, decreasing again with increase in acid concentration to 20% in concentrated acid. Lead shows maximum extraction from 1·5*M* acid, decreasing to nothing at 10*M*. Tellurium is quantitatively extracted from hydrochloric acid solutions between 4 and 6*M* and was readily back-extracted with 0·5*M* acid. The extraction of tin commences at 0·5*M* hydrochloric and increases with increase in acid concentration, reaching a maximum between 5 and 6*M*, then decreasing above 6*M* acid; back-extraction using 1*M* nitric acid is recommended, dilute hydrochloric and sulphuric acids being stated as unsuitable. Quadrivalent vanadium does not extract from hydrochloric acid solutions, whereas up to 90% of quinquevalent vanadium may be extracted from 6*M* acid. When the acid concentration is greater than 6*M*, reduction of the vanadium occurs and extraction decreases.

Using Amberlite LA.1 as a 10% solution in kerosene, Nakagawa[12,13] has investigated the extraction of iron(III), nickel, cobalt, zinc, aluminium, titanium, arsenic, antimony and bismuth from hydrochloric acid solution. A summary of his results is given in Table IV.

TABLE IV.—EXTRACTIONS USING 10% AMBERLITE LA.1 IN KEROSENE

Element	Optimum HCl range, *M*	Extent of extraction, %
Aluminium(III)	—	Negligible
Arsenic(III)	8–11	92
Arsenic(V)	—	No extraction
Antimony(III)	1–4	Almost quantitative
Antimony(V)	>6	Quantitative
Bismuth(III)	0·3	Quantitative
Cobalt(II)	8	35
Iron(III)	6–10	Quantitative
Nickel(II)	—	No extraction
Titanium(IV)	12	10
Zinc(II)	2–3	90

Tervalent arsenic extracts from solutions greater than 4*M* in hydrochloric acid, a maximum extraction of 92% occurring in 8–11*M* acid. Tervalent antimony is almost quantitatively extracted from 1–4*M* acid solutions, extraction decreasing with increase in hydrochloric acid concentration. The extraction of quinquevalent antimony is, however, facilitated by an increase in acid concentration and only becomes quantitative from solutions greater than 6*M*. Bismuth extraction is complete from 0·3*M* acid; increasing the hydrochloric acid concentration results in decreasing extraction until at 10*M* acid no extraction occurs. It is recommended that tervalent antimony and bismuth be back-extracted using 0·5*M* citric acid, and quinquevalent antimony with 1*M* sodium hydroxide, but not with mineral acids. Cobalt extraction starts from solutions more than 5*M* in acid, but maximum extraction at 8*M* acid is only about 35% complete. No extraction of titanium occurs from solutions below 8*M* in acid and only about 10% from concentrated hydrochloric acid solutions. Zinc extraction is maximum at 2–3*M* acid, decreasing with increase in acid concentration.

The extraction data given by Nakagawa provide an excellent example of the parallelism which exists between liquid and resinous ion exchangers. The reader can qualitatively extend the data given in Tables III and IV by reference to the more comprehensive work on anion exchange in chloride media by Kraus and coworkers.[56]

Amberlite LA.1 has been used by Ishibashi and Komaki[14] for the determination of zinc in aluminium alloys. The zinc, present at about the 5-mg level, is extracted into a 15% solution of Amberlite LA.1 in kerosene from 6*M* hydrochloric acid. The procedure is to dissolve the sample in 6*M* hydrochloric acid and hydrogen peroxide, then extract the zinc with Amberlite LA.1/kerosene. The zinc is back-extracted into the aqueous phase using 0·3*M* nitric acid, the solution made ammoniacal and triethanolamine and potassium cyanide added to mask iron and copper. Finally, the zinc is demasked using formaldehyde and titrated with standard EDTA.

For the determination of zirconium in cast iron, Green[15] employed a 4% solution of Amberlite LA.1 in chloroform. The precedure here is to dissolve the sample in sulphuric acid in the presence of a small amount of sodium fluoride. After mercury cathode separation, hydrogen peroxide is added and zirconium extracted with Amberlite LA.1/chloroform. The zirconium is back-extracted with hydrochloric acid and finally reacted with Pyrocatechol Violet for spectrophotometric measurement. Titanium and vanadium will be partially extracted by the exchanger under these conditions and a correction has to be applied if either or both are present.

Using the same exchanger, 4% of Amberlite LA.1 in chloroform, Green[16] has determined uranium in cast iron. The sample is dissolved in sulphuric acid solution and extracted directly with the ion exchanger. Under the conditions used, apart from the uranium, any niobium, tantalum and zirconium present will be extracted, along with a small quantity of iron. Back-extraction of the organic phase with sodium carbonate results in precipitation of these elements, while the uranium is extracted as the water-soluble uranyl-carbonate complex, $UO_2(CO_3)_3^{4-}$. After filtration, the uranium in the filtrate is reacted with hydrogen peroxide to yield the yellow peroxy complex, which is measured spectrophotometrically.

The use of Amberlite LA.1 has been described for the determination of zinc in bauxite.[17] Fifty ml of a 25% solution of the exchanger in xylene can be used to extract up to 5 mg of zinc from 1-g samples of bauxite. Despite the high concentration of exchanger, the organic phase can be fed directly to the burner of a Perkin-Elmer 214 atomic absorption spectrophotometer to complete the determination.

In an investigation into the separation and determination of chromium sesquioxide in chrome ores and refractories, Bennett and Marshall[18] used both Amberlite LA.1 and LA.2. The extraction of chromium from sulphuric acid solution, as the dichromate ion, increased with increasing acid concentration. However, at higher acid concentrations, increasing reduction of the sexivalent chromium took place. Because

Amberlite LA.2 is the more basic of the two exchangers and shows less tendency to emulsify, it was chosen for use in the final method. For decomposition of the sample a fusion is made using 7 g of anhydrous sodium carbonate and 2·5 g of boric acid with 0·5 g of sample. The cooled melt is extracted with dilute sulphuric acid and dilute aqueous ammonia added until a faint permanent precipitate forms. This precipitate is just dissolved by addition of dilute sulphuric acid and the solution extracted using a 10% solution of Amberlite LA.2 in chloroform. After two 25-ml extractions with the exchanger, further sulphuric acid is added to the aqueous phase and a third extraction made with 25 ml of exchanger. The extracts are combined and back-extracted using $1M$ potassium hydroxide. After acidification and reduction with sulphite, the chromium is reacted with EDTA and the determination completed by spectrophotometric measurement of the violet complex at 550 mμ. Under these conditions, other constituents of chrome ores and refractories, such as iron, titanium, manganese and silicon, are in no way affected by the ion-exchange separation and the aqueous phase can be used for their determination after being washed with chloroform.

The behaviour of tin(IV) and lead ions in extraction from hydrochloric acid solutions with a xylene solution of Amberlite LA.2 has been studied by Nakagawa.[19] Tin(IV) can be extracted from hydrochloric acid solutions between 5 and $9M$ up to 98%; lead extraction is about 40% from $2M$ acid, decreasing rapidly with increasing acid concentration to become negligible at concentrations above $8M$. A method for the separation of tin and lead was suggested in which the solution of the metal ions is adjusted to between 7 and $8M$ in hydrochloric acid. Two extractions are made using a 10% solution of Amberlite LA.2. The combined organic phases are then washed with fresh 7–$8M$ hydrochloric acid to remove traces of lead, and the tin returned to the aqueous phase by stripping with three consecutive volumes of $0{\cdot}5M$ nitric acid.

Hirano, Mizuike and Iida[20] have employed Amberlite LA.2 as a 10% solution in xylene for the determination of traces of cadmium in thorium compounds. The sample, containing about 10 g of thorium, is dissolved in hydrochloric acid and sodium fluoride solution, evaporated almost to dryness after addition of nitric acid, then taken up with 5 ml of concentrated hydrochloric acid and 35 ml of water. The cadmium in the solution is extracted with two 10-ml volumes of the exchanger. The combined extracts are washed twice with small volumes of $1M$ hydrochloric acid to remove iron and the cadmium back-extracted using two 5-ml volumes of $2M$ nitric acid. The cadmium in the extract is then determined polarographically. It is claimed that the separation can be applied to cadmium determinations as low as 0·01 ppm with a relative error of less than 10%.

Unpublished work, reported to the author,[59] shows that macro quantities of lead may be extracted using a 20% solution of Amberlite LA.2 in hexone. From a 100-ml volume of solution containing the equivalent of 0·13 g of PbO, 5 ml of concentrated hydrochloric acid and 1·5 g of potassium iodide, two extractions with the exchanger followed by one extraction with hexone alone will achieve a lead extraction of over 99%. The concentration of acid and iodide appears to be rather critical. Presumably, other metal iodides, such as those of tin, antimony, bismuth and cadmium, could be extracted under similar conditions.

Although the Amberlite exchangers have received the widest attention, other amines have proved of great value for certain separations. It has been shown by

Baeckmann and Glemser,[21] using a solution of a tertiary amine such as tribenzylamine (TBA) in chloroform, that it is possible to separate iron(III) chloride from elements which do not form anionic chloro complexes, such as aluminium, silicon, zirconium, titanium, hafnium, thorium, niobium, tantalum, nickel and alkali and alkaline earth metal ions. The extraction is made from 5*M* hydrochloric acid solution using a 0·2*M* solution of TBA in chloroform, when a quantitative separation can be achieved. The iron may be back-extracted into the aqueous phase using hydrochloric acid solutions less than 0·5*M*.

The separation of niobium and tantalum has been achieved by Ellenburg, Leddicotte and Moore,[22] using TBA in chloroform. Niobium can be extracted easily with equal volumes of aqueous and organic phases, whereas tantalum extraction was minimal. The extraction of niobium is dependent on the concentration of TBA in the organic phase—the distribution coefficient rising from 0·20 using 1·25% TBA to 74·4 using 8% TBA. The corresponding values for tantalum are 0·003 and 0·002, respectively. The concentration of acid is quite critical. Using 8% TBA in chloroform, practically no extraction occurs below 8*M* hydrochloric acid. At 9*M* acid the Kd value is 5·05 for niobium and 0·0013 for tantalum; from 11*M* hydrochloric acid the Kd values are 74·4 and 0·0025, respectively. When methylene chloride is used instead of chloroform the extraction is even better, niobium giving a Kd of 80·5 and tantalum 0·0023 from 11*M* hydrochloric acid. The reason for the success of the separation achieved under these conditions is explained by 'the extraction of niobium as an oxychloride complex of the type $H(NbOCl_4)$ or $H_2(NbOCl_5)$, while neither chlorotantalates nor oxychloride complexes of tantalum are presumed to exist in aqueous solution'. The investigation was extended to extraction from sulphuric acid solutions. Quantitative separation of tantalum and niobium is possible from 4·5*M* acid solution. The acid concentration is stated to be very critical. Both niobium and tantalum are extracted from oxalic acid solutions using TBA in chloroform and methylene chloride; on the other hand, if the solvent is changed to benzene, toluene, xylene or carbon tetrachloride, no extraction of either metal takes place.

Using a 5% solution of methyldioctylamine (MDOA) in xylene, Leddicotte and Moore[23] showed that niobium and tantalum could be separated satisfactorily. The radioactive isotopes ^{95}Nb and ^{182}Ta were used in the investigation. From hydrochloric acid solutions the extraction of tantalum is only 0·25% at 3*M* acid concentration, rising to only 1·4% in concentrated acid. With niobium, on the other hand, extraction is 2·4% at 3*M* hydrochloric acid with the percentage extraction increasing rapidly above 6*M* acid to reach over 99% at 8*M*. From nitric acid solutions neither niobium nor tantalum extracts appreciably up to 10·6*M*; from sulphuric acid solution up to 12*M* very little niobium extracts, but tantalum extraction is appreciable at 2*M* sulphuric acid, decreasing with increase in acid concentration.

Following the investigation into these separations for tantalum and niobium using MDOA and TBA, Mahlman, Leddicotte and Moore[24] examined the extraction of chromium, manganese, iron, nickel, copper, zinc and cobalt. In each case the course of the extraction was followed by using radioactive materials. From aqueous hydrochloric acid solutions using an 8% solution of MDOA in trichloroethylene, chromium extraction is only about 2%, and nickel less than 1%, irrespective of the acid concentration from 0·1 to 10*M*. Very little manganese is extracted below 5*M* hydrochloric acid and only 32% from 10*M*. Iron extraction becomes appreciable above about

0·5M and reaches a maximum at 94/95% between 4 and 5M acid, remaining at more than 90% even in 10M hydrochloric acid. Cobalt extraction is less than 2% in 3M acid, rising rapidly to 85% in 10M acid. Zinc, on the other hand, extracts readily from 0·5M acid, with quantitative extraction occurring from 2 to 10M acid. When chloroform is substituted for the trichloroethylene, cobalt does not extract until 8M acid, while zinc gives a maximum extraction of 85% at 3M acid. When the organic diluent is changed to xylene, cobalt extraction does not reach 2% until 4M hydrochloric acid, and is only 21% in 10M acid. Zinc again shows maximum extraction in 3M acid—over 99%, with over 95% extraction taking place from all solutions between 1 and 10M. When TBA is used in place of MDOA, maximum zinc extraction of 72% again occurs at 3M acid with negligible cobalt extraction occurring below 6M acid.

Other amines which have been used by a number of workers are tri-iso-octylamine and tri-n-octylamine. Marchart and Hecht[25] have examined the extraction behaviour of tantalum and niobium with tri-iso-octylamine from various acids and acid mixtures. The distribution coefficient is dependent on the acid concentration and on the nature of the complexing agent used. A method is given for the separation of the two metals from nitric/hydrofluoric acid solution.

The distribution of septivalent rhenium between nitric acid solutions and tri-iso-octylamine has been investigated by Kertes and Beck.[26] Variation in the rhenium molarity in the organic phase shows that the species extracted is free perrhenic acid, $HReO_4$.

Using tri-iso-octylamine hydrochloride, Lorenzini, Stoppa and Barbieri[27] separated gram-quantities of uranium from solutions of 8M hydrochloric acid before the spectrographic determination of the rare earth elements. A 6-g sample of uranium metal is dissolved in 50 ml of 8M hydrochloric acid and extracted with five 100-ml portions of 0·3M tri-iso-octylamine hydrochloride in a xylene/octanol mixture (19:1). Any iron present is extracted with the uranium.

White, Kelly and Li[28] have converted tri-n-octylamine (TOA) to its hydrochloric and perchloric salts before an investigation into the chloride complexes of iron(III) and indium(III). The tertiary amine is dissolved in benzene and equilibrated with equal volumes of 1M hydrochloric and perchloric acid to convert it to the appropriate salt. The amine itself is a light yellow colour; its hydrochloride and perchlorate salts in benzene are light yellow and slightly pink, respectively. The investigation was made using the radioactive materials ^{59}Fe and ^{114}In; the aqueous phase contained the metal ion in a concentration of the order of $10^{-7}M$ and varying concentrations of hydrochloric acid and/or perchloric acid. The organic phase contained the TOA salt in benzene and in each case was equilibrated with an equal volume of the aqueous phase to be used, without the radioisotope. Equal volumes of aqueous and organic phases were shaken for a number of hours at 25 ± 0·5°, then allowed to settle for 1 hr before measurement of the radioactivity of each phase. No extraction of iron or indium occurs from perchloric acid solutions less than 2M with no chloride present, indicating that the perchlorate ion does not form anionic complexes with either iron or indium in the organic phase. The distribution coefficient (defined as the concentration of metal ions in the organic phase divided by the concentration of metal ions in the aqueous phase) for both iron and indium are second power dependent on the

TOA/hydrochloric acid concentration in the benzene phase, indicating that the negatively charged complexes $FeCl_5^{2-}$ and $InCl_5^{2-}$ are formed in the organic phase.

The distribution of sulphuric acid between water and a benzene solution of TOA and tri-n-hexylamine (THA) has been investigated by Verstegen and Ketelaar.[29] Assuming that the organic activities of the amine salts, $(TOAH)_2SO_4$ and $(THAH)_2SO_4$, are equal to concentrations, then the law of mass action describes the equilibrium until the amine salt exceeds a certain value. The heat and entropy of the formation of $(TOAH)_2SO_4$ have been calculated and the equilibrium leading to the formation of $(THAH)_2SO_4$ studied at 25°. Finally, the relative basic strengths of tertiary amines, on the basis of infrared measurements of the proton-accepting properties, are discussed. It is emphasised by the authors that the results obtained using infrared measurements may only be interpreted as showing a certain trend because of small variation in the proton-accepting property. Furthermore, it is certainly not the only point governing the relative basicity of the amines.

An extensive investigation[30] has been made into the extraction of uranium from aqueous sulphate solutions by long-chain aliphatic primary, secondary and tertiary amines in various organic diluents. Tertiary amines have a remarkable preference for uranium over the other elements normally found in uranium leach liquors. Only molybdenum is extracted to any great extent. The extraction coefficients for uranium from sulphate solutions at a pH of about 1 are directly proportional to the concentration of the amine in the organic phase (see figures quoted earlier for Amberlite LA.1). At the same time, the extraction coefficients are dependent on temperature, pH, sulphate concentration and concentration of other anions in the aqueous phase. The back-extraction of uranium can be accomplished using dilute hydrochloric acid, sodium carbonate, sodium hydroxide or aqueous solutions. Using aqueous ammonia, the uranium is precipitated as it is returned to the aqueous phase. Again, there is a close parallel with the studies on ion exchange, such as those reported by Burstall *et al.*[58]

The tertiary amine didodecenyl-n-butylamine (Amberlite XE-204) has not been investigated to a great extent. However, Dono, Nakagawa and Wada[31] have employed it for the separation of micro amounts of nickel in cobalt. Approximately 95% of the cobalt can be extracted from an 8*M* hydrochloric acid solution, but nickel does not extract from hydrochloric solutions of any concentration.

Direct spectrophotometric determinations after liquid anion-exchange

Using a 1% solution of TBA in chloroform, Fasolo, Malvano and Massaglia[32] have extracted chromium(VI) from 1*M* hydrochloric acid solutions. The chloroform extracts can be measured spectrophotometrically to obtain the chromium content. Maximum absorption occurs at 355 and 458 mμ. Only gold (100%), antimony ($>90\%$) and mercury ($>95\%$) give appreciable extraction under the conditions used. Negligible extraction ($<1\%$) occurs for copper, cobalt, nickel, zinc, iron, chromium, manganese, cadmium, arsenic, uranium, cerium, molybdenum, rare earths and alkaline earths.

Direct spectrophotometric determination of the green cobalt complex in the organic phase, after extraction of cobalt thiocyanate using a 20% of TOA in carbon tetrachloride, is reported by Selmer-Olsen.[33] The absorption curve shows two maxima (340 and 627·5 mμ). Bivalent manganese, nickel and zinc give no colour in the organic layer and do not interfere, while iron gives an absorption maximum at 475 mμ and practically no absorption at 627·5 mμ. It is, therefore, possible to determine small amounts of iron and cobalt in the presence of each other.

LIQUID CATION EXCHANGERS

Coleman, Blake and Brown[3] listed 24 liquid cation-exchange materials, but to-date only two of these have been used to any extent. These are di-(2-ethylhexyl)orthophosphoric acid (D2EHPA, DEHPA or HDEHP) and dinonylnaphthalene sulphonic acid (DNS).

DNS is obtained from the manufacturers as an approximately 48% solution in n-heptane, and is a mixture of isomers resulting from the sulphonation of dinonylnaphthalene, the dinonylnaphthalene being made by controlled alkylation of naphthalene with nonene. It is a monobasic acid with only slight solubility in water but readily soluble in many organic solvents. White, Tang and Li[34] analysed the material by extraction of a known volume of the solution in heptane with standard potassium hydroxide solution, followed by titration of the aqueous phase with standard hydrochloric acid. Kaufman and Singleterry[35] have demonstrated micelle formation by DNS in moist benzene, and White *et al.*[34] inferred from this 'that DNS in moist heptane may also exist as the polymer, $(DNS)_x$.'

The behaviour of DNS as a liquid cation exchanger has been examined by White, Tang and Li.[34] Using ^{60}Co, ^{54}Mn, ^{59}Fe, ^{114}In and ^{65}Zn as radioactive tracers, extractions were made from an aqueous phase, containing the metal radioisotope at a concentration of $10^{-6}M$, into a heptane solution of DNS in concentrations of the order of 10^{-3} to $10^{-4}F$. The heptane/DNS reagent was shaken for a number of hours with an equal volume of 0·1*M* perchloric acid before use. Extractions were made using equal volumes of aqueous and organic phases of Co^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+} and In^{3+} as the perchlorates with a varying concentration of perchloric acid to obtain the desired pH, at a temperature of 25 ± 0·5°. After shaking for a number of hours, the two phases were allowed to settle for 1 hr and the activity of the metal ion in each phase measured.

The results show that the distribution coefficients of the bivalent and tervalent ions are inversely second power and third power, respectively, dependent on the pH of the aqueous phase and first power dependent on the DNS concentration of the heptane phase. At the same time, experiments were made to determine the formation constants of the indium(III) complexes of glycolate and bioxalate and the cobalt(II) complex of bioxalate. The formation constants obtained using DNS agree with the values obtained using a resinous cation exchanger.

The stability constants of the iron(III) and indium(III) chloride complexes were investigated by White, Kelly and Li[28] using DNS and radioisotopes ^{59}Fe and ^{114}In. Using metal ion concentrations of about $10^{-7}M$ and varying concentrations of hydrochloric and/or perchloric acid, extractions were carried out using equal volumes of aqueous and organic phases. In each case the organic phase was pre-equilibrated with an equal volume of the aqueous phase to be used, without the radioisotope. The total hydrogen ion concentration in each experiment was kept constant while the ratio of hydrochloric and perchloric acids varied. The solutions were shaken at 25 ± 0·5° for a number of hours, then allowed to settle for 1 hr before measuring the radioactivity of each phase.

A table is given showing the decrease in distribution coefficient for iron(III) with increase in hydrochloric acid concentration and corresponding decrease in perchloric acid concentration to maintain the total acid at 1*M*. The Kd value at 1*M* perchloric acid is 3·01 and on subsequent substitution of hydrochloric acid for the perchloric acid the Kd value becomes 0·65 at 0·8*M* hydrochloric acid/0·2*M* perchloric acid. By assuming that there is no complexing of M^{3+} and ClO_4^-, the stability constant for the reaction $M^{3+} + Cl^- \rightarrow MCl^{2+}$ was calculated by the method of White *et al.*[34]

Good agreement was found for iron between the stability constants determined using DNS and the values in the literature obtained spectrophotometrically. The stability constant of the $FeCl^{2+}$ complex at ionic strengths varying from 0·2 to 1·0 is independent of whether H^+ or Na^+ is the cation associated with the perchlorate ion. With the indium(III) complex, the substitution of Na^+ for H^+ as the cation associated with the perchlorate ion decreases the value of the stability constant.

D2EHPA has been employed by McHenry and Posey[36] for the separation of strontium-90 and calcium. Calcium is extracted into the organic phase while the strontium remains in the aqueous phase to an extent greater than 95%. The effects of the addition of acetic acid, alcohol and 2-ethylhexanol on the recovery of calcium and strontium and on their distribution coefficients were investigated.

Using the same reagent, Butler and Ketchen[37] separated cerium-144 and yttrium-91 from other rare earth fission products, producing a highly pure ^{144}Ce in good yield. The extractions were made from nitric acid solution containing citric acid and the cerium was oxidised to the quadrivalent state with permanganate before extraction.

Using a D2EHPA solution in toluene, Peppard *et al.*[38] employed fractionation extraction of the lanthanides and yttrium from solutions containing various anions—nitrate, chloride and sulphate. The extracted lanthanide species do not contain any of the anion associated with the lanthanide in the original solution. Once this was established the rest of the investigations were carried out from hydrochloric acid solutions. Using radioisotopes it was found that, under the experimental conditions used, the distribution coefficients are directly third power dependent on the concentration of D2EHPA in the organic phase and inversely third power dependent on the hydrogen ion concentration of the aqueous phase. A further paper by Peppard *et al.*[39] examined the relative effectiveness of mono- and di-orthophosphoric esters for the extraction of the rare earths.

Using a 4% solution of D2EHPA in toluene, Arden[40] has determined the radioisotope ^{95}Zr in fission products. These products are allowed to cool for a minimum period of 15 days, then taken into solution with mineral acids, such as nitric, hydrochloric and sulphuric. A suitable aliquot of the solution is taken, such that the activity will not be less than 200 cpm. Niobium, iron and iodine carriers are added, together with hydrogen peroxide, and the solution is extracted with carbon tetrachloride. The organic phase containing any radio-iodine is discarded and the aqueous phase extracted with the toluene/D2EHPA. The aqueous phase is then discarded and the organic phase is extracted with potassium thiocyanate solution to remove any radio-iron. The organic phase, which contains the radio-zirconium, is then counted using a γ-scintillation counter.

The determination of total radio-strontium in milk using D2EHPA in toluene has been described by Butler.[41] The major problem in the analysis of milk for total radio-strontium is the removal of the large quantities of calcium that are present before counting. Using a 20% solution of D2EHPA in toluene, calcium is removed from hydrochloric acid solution by one extraction at pH 3·6–3·8, followed by a second extraction at pH 2·6–2·8, using equal volumes of aqueous and organic phases. These extracts are discarded and the strontium extracted at pH 4·8–5·0. The strontium is then back-extracted from the organic phase using 3*M* nitric acid and after suitable treatment the β-count of the strontium determined.

At a Symposium on Solvent Extraction Chemistry held at Gatlinburg, U.S.A., in 1962, a series of papers covering the theory and use of D2EHPA as an ion-exchanger was presented. A number of these papers have now been published in the open literature.[6] The reader who is about to use this reagent for the first time is recommended to consult these papers in view of the valuable information they contain.

At the same Symposium a paper on extraction with sulphur-containing organophosphorus compounds was presented by Handley.[42] Both mono- and di-substituted sulphur derivatives of the alkylphosphoric acids were investigated. In general, these new reagents extract from mineral acid solutions those metal ions which form insoluble sulphides. Because of their stability and wide range of acid tolerance it may be possible to use these reagents for many purposes where at the present time xanthates and diethyldithiocarbamates are employed.

CHROMATOGRAPHIC SEPARATIONS USING LIQUID ION EXCHANGERS

Chromatographic separations of a number of cations by means of paper treated with liquid ion exchangers have been reported by Testa and Cerrai. In the first report[43] the paper was treated with a 0·2*M* solution of TOA. Paper treated with TOA behaves very much like a film of anionic resin: it retains the chloride, nitrate and sulphate complexes of the various elements in accordance with the strength of the complex itself. The cations were used in concentrations of 20–50 μg in hydrochloric acid solution for each spot and development was carried out with appropriate reagents, such as potassium thiocyanate for iron(III), dimethylglyoxime for nickel and 8-hydroxyquinoline for cobalt. Using circular chromatography and 4*M* hydrochloric acid for elution, these three ions can be separated satisfactorily. Nickel follows the solvent front (R_f 0·97) because it is not complexed by hydrochloric acid and hence not retained by the amine. Cobalt is partially complexed and gives an R_f value of 0·50, while iron is completely complexed (R_f 0) and is retained in the original spot by the amine. Similarly, using 10*M* hydrochloric acid, uranium (R_f 0), zirconium (R_f 0·35) and thorium (R_f 0·95) can be separated or uranium, zirconium and titanium (R_f 0·85). Many other separations are possible using hydrochloric acid of suitable strengths. These include iron(III), copper and aluminium using 1*M* acid; uranium, vanadium and titanium using 3*M* acid; zinc and manganese using 3*M* acid; zinc, cobalt and manganese using 4*M* acid; zinc, manganese and nickel using 10*M* acid. Separation of zirconium (R_f 0·25) and hafnium (R_f 0·80) is made using 8*M* hydrochloric acid plus 5% concentrated nitric acid. When a 0·2*M* sulphuric acid solution is used, uranium and nickel can be separated from iron and copper, and using 0·5*M* sulphuric acid separation of molybdenum from iron, copper and nickel is possible.

Descending chromatography was used for the separation of some cation mixtures, such as zinc, cobalt and manganese, uranium, zirconium, thorium, vanadium and titanium. By judical selection of the strength of hydrochloric acid for elution, satisfactory separations were made of these mixtures.

The second report[44] dealt with the separation of uranium, thorium and lanthanum. In this case the chromatographic paper was treated with benzene solutions of various concentrations of TOA and elution was made using nitric acid, lithium nitrate, sodium nitrate, ammonium nitrate, calcium nitrate and aluminium nitrate. Lanthanum is not retained by the amine and so moved with the solvent front, while thorium and uranium form well defined spots. Lowering the TOA concentration on the paper effects a considerable increase in the R_f values of both thorium and uranium. Increasing the strength of the nitrate solution for elution decreases the R_f values for all three cations.

A third report[2] examined the use of TOA-cellulose in chemical separations. Whatman No. 1 cellulose powder was impregnated with $0{\cdot}1M$ TOA in benzene and then heated for 2 hr at 85° to volatilise the benzene solvent. The treated cellulose was crushed in a mortar, then packed into a column, fitted at the bottom with a fritted glass disc. This column was then used in a similar manner to a column of ion-exchange resin. Nickel, cobalt and iron can be separated by elution with hydrochloric acid; similarly, thorium, zirconium and uranium. The authors admit that the exchange capacity of this type of column is only 25–30% of that of the common resin but claim a number of advantages:

(1) Because of the white colour of the column the position and movement of coloured zones can be easily followed.
(2) Because the active functional groups are concentrated at the surface of the powder grains and the grain size is very small, the column has a high ability to fix large molecules, which often cannot penetrate the complex structure of anionic resins.
(3) Very narrow elution peaks are obtained.
(4) When working with radioactive tracers the column can be easily burned and the residue conveniently obtained for radioactive counting; the resins are less easily burned.

The chromatographic separation of the rare earths using paper treated with TOA and elution with lithium nitrate has been studied by Testa.[45] Previously reported work suggested that the rare earth elements formed anionic complexes in a concentrated solution of an alkaline nitrate. Based on this, Testa determined the R_f values for a number of rare earth elements, for various concentrations of lithium nitrate as eluting solution, using chromatographic paper treated with $0{\cdot}2M$ TOA in benzene. From these R_f values a number of separations of the rare earth elements was shown to be possible. The R_f values obtained increase on adding nitric acid to the lithium nitrate for elution, indicating that the presence of free nitric acid lowers the formation of the complex. The spots from the various elements were developed by means of a 1% solution of 8-hydroxyquinoline in 1:1 water/alcohol. On exposure of the paper strips to ammonia vapour the spots became clearly visible.

A further study of Cerrai and Testa[46] involved the separation of the rare earth elements on chromatographic paper treated with a $0{\cdot}1M$ solution of D2EHPA in cyclohexane. The R_f values for 9 rare earths (lanthanum, cerium, praseodymium, samarium, europium, gadolinium, dysprosium, erbium, ytterbium) and 7 additional elements (yttrium, scandium, thorium, uranium, zirconium, iron, aluminium) as functions of the molarity of the hydrochloric acid elutriant are given. The spots were developed using a 1% solution of 8-hydroxyquinoline in 1:1 water/alcohol solution. A relationship was established between the quantity log $(1/R_f - 1)$ and (1) the atomic number of the element, (2) the molarity of the acid used as elutriant, (3) the molarity of the solution with which the paper is treated, and (4) the operating temperatures. Under the same conditions, the R_f values increase as the atomic number decreases. For a given element, the R_f value increases with the strength of the acid used for elution and with the operating temperature, and it decreases with the concentration of D2EHPA on the paper. Examples are given of the chromatographic separation of the rare earth elements from each other and from the other 7 elements mentioned previously.

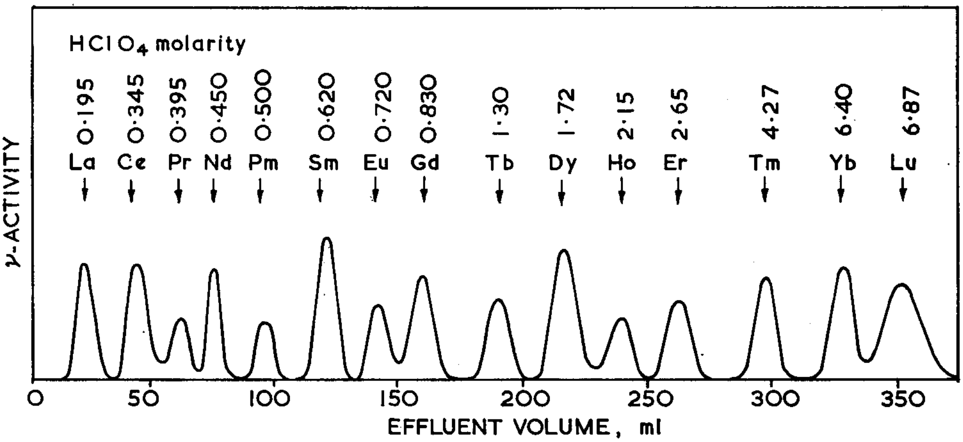

FIG. 2.—Separation of the rare earths by gradient elution from a Corvic/HDEHP column.[47]
(*Reproduced by courtesy of Macmillan & Co. Ltd.*)

The chromatographic separation of the rare earth elements using D2EHPA and reverse-phase partition chromatography has been described by Pierce *et al.*[47,48,49] A chromatographic column impregnated with D2EHPA was prepared using poly-(vinyl chloride/vinyl acetate) copolymer ('Corvic', Imperial Chemical Industries Ltd.) as supporting medium. Ten g of the copolymer (100–150 mesh) were mixed with 10 ml of solution containing 5 ml of chloroform plus 3 ml of toluene plus 2 ml of D2EHPA. The organic solvent was evaporated off and the resulting powder slurried in 0·002M perchloric acid and made into a column of the required size. The temperature of the column was thermostatically controlled at 60° and a flow rate of 2·0 ml.cm^{-2}.min^{-1} used throughout the experiments. It was shown that the separation of the rare earth element is possible using elution with perchloric acid. Separation of certain combinations of the rare earths, such as cerium with praseodymium and europium with gadolinium, proved difficult when perchloric acid of constant strength was employed for elution. Gradient elution using perchloric acid of gradually increasing strength is very successful in separating the rare earth series, the elements being eluted successively in the order of increasing atomic number. In order to check the separations, radioactive earths were used in dilute perchloric acid solution and the effluent from the column was passed through a γ-scintillation flow counter. The elution peaks were identified using a γ-spectroscope and the acidity of the eluate at the peak maxima was determined by titration with standard alkali. Fig. 2 illustrates the results obtained using gradient elution for separation of the rare earths on a Corvic/D2EHPA column.

Sastri and Rao[50] have described the use of paper impregnated with DNS for chromatographic separations. The paper was treated with a $0{\cdot}1M$ solution of DNS in n-heptane and the solvent removed by blowing hot air. The chromatograms were obtained using the ascending technique and the solvent front was allowed to move through a distance of 18 cm. More than 20 metal ions were examined using nitric and hydrochloric acids as elutriants at strengths between 0·1 and $1{\cdot}0M$. The R_f values increase with increase in the strength of the acid used to elute, and the R_f values for hydrochloric acid are somewhat greater than for nitric acid. The values obtained are in agreement with those expected from the cation-exchange mechanism. A number of separations were shown to be possible, *e.g.*, aluminium and beryllium; copper and cadmium; iron, titanium and vanadium; indium, gallium and zinc; calcium, barium and magnesium; in each case using $0{\cdot}25M$ hydrochloric acid.

NEUTRAL CO-REAGENTS

Reagents such as tri-n-butylphosphate and tri-n-octylphosphine oxide have been classed as 'neutral co-reagents' by Coleman *et al.*[3] They are frequently used for extraction of metal ions from aqueous solution. It is not the intention of this review to cover the use of these extractants. The reader is referred to the summary of much of the earlier work carried out with neutral co-reagents by Morrison and Freiser[51] and a more recent review by White and Ross.[52]

MISCELLANEOUS

The determination of amines and alkylphosphates in kerosene solutions, used for the extraction of uranium, has been reported by Ashbrook.[53] For the determination of an amine the kerosene is shaken with calcium hydroxide, when the sulphuric acid present is precipitated as calcium sulphate and the uranium absorbed on the calcium hydroxide. The solids are then removed by filtration and the amine determined in the filtrate by titration. If alkylphosphates are present it is necessary to extract the uranium first with 20% sulphuric acid, then to shake the kerosene with calcium acetate. The amine is titrated in chloroform solution with a dioxan solution of perchloric acid using Thymol Blue as indicator. For the determination of an alkylphosphate the kerosene is shaken with sodium methoxide. This precipitates the sulphuric acid as sodium sulphate, which is insoluble in chloroform. Excess methoxide is back-titrated with perchloric acid to the blue/yellow end-point (pH 8·9) of Thymol Blue. The titration with perchloric acid is then continued to the yellow/red end-point of the indicator (pH 1·7). At this stage both amine and alkylphosphate are titrated, and the difference between this volume of perchloric acid and that used to titrate the amine alone is equivalent to the amount of alkylphosphoric acid.

Damodaran[54] has recently found that a chloroform solution of tetra-n-hexylammonium iodide will extract the highly coloured anion $[Co(NH_3)_2(NO_2)_4]^-$ of Erdmann's salt, to give a deeply coloured liquid anion exchanger. Such a solution had been used to study exchange equilibria for a number of anions. Typical results are

(a) $F^- < Cl^- < Br^- < I^-$,

(b) $Cl^- < ClO_3^- < ClO_4^-$,

(c) $BF_4^- < ClO_4^- < IO_4^- < ReO_4^- < MnO_4^-$.

Anions such as SO_4^{2-} and PO_4^{2-}, which carried more than unit charge, are not extracted at all. The concentration of erdmannate ion displaced into the aqueous phase by the competing anion can be determined spectrophotometrically and so used for indirect determination of the anion in question.

The determination of perchlorate ion using this indirect technique with the erdmannate ion has been described by Clifford and Irving.[55] Interference of many other ions is overcome by pretreatment of the solution with silver sulphate. The interference of chlorate can be serious; when the ratio of ClO_3^- to ClO_4^- is 10:1 the error is 5%, and at a ratio of 100:1 it is about 35%. The error can be reduced by reduction of the chlorate ion to chloride using sulphurous acid or iron(II) sulphate. If the necessary constants are known a suitable correction for the chlorate ion can be calculated.

The use of reagents of the Erdmann or Morland $[Co(NH_3)_2(SCN)_4]^-$ type opens up some interesting possibilities and will undoubtedly extend the use of liquid anion exchange.

FUTURE OF LIQUID ION EXCHANGERS

It is not because of low potentiality that liquid ion exchangers have not been accorded the attention of other extraction systems. As already pointed out, the use of liquid ion-exchange extraction dates from 1948, compared to, say, resinous ion exchange, which may be said to have started in 1935 with the discovery by Adams and Holmes of the ion-exchange properties of certain synthetic resins.[57]

The reasons for the lack of attention to liquid ion exchangers are not easily defined. Partly the cause may be lack of knowledge of the fundamental principles of the technique, and partly the belief that extractions with such materials are only an extension of normal solvent extraction processes and not a separate technique at all. The tendency for emulsion formation between the aqueous and organic phases may be a contributory cause, again because of lack of basic knowledge to enable this to be avoided. In most cases the need for stripping the organic extract to complete the analysis, compared with the ease with which the extracts from chelate extractions may be utilised directly for spectrophotometric measurement, has undoubtedly contributed to lack of interest in their use. On the other hand, the rapidity with which the ion-exchange process is completed using liquid exchangers, instead of resinous exchangers, does not appear to have been of such wide interest to the users of ion exchange as might have been expected. This is probably because many analytical separations using resinous exchangers are made by the techniques of 'selective elution' or 'frontal analysis'.

What then is needed to make the technique of liquid ion exchange acceptable to more analysts?

1. Greater basic knowledge of the principles involved.
2. Some means of assessing the relative 'strengths' of the exchangers.
3. Investigations into the change in extraction properties of the exchangers which occurs when the organic diluent is changed.
4. Greater selectivity in separations, *e.g.*, by choice of a suitable exchanger for the particular separation or by a suitable selective back-extraction technique.
5. Easier ways of employing the organic phase directly for determination of the extracted ions.

The possibilities of liquid ion exchangers are slowly becoming apparent as analytical methods employing these materials are published. Bennett and Marshall[18] pointed out the tedious nature of the current methods for the analysis of chrome ores and chrome-bearing materials and the discrepancies which can occur between laboratories analysing these materials. By employing liquid ion exchange the time taken in analysis was reduced appreciably and reproducibility improved.

Green[16] showed that liquid ion exchange could be made to work directly for the separation of uranium in cast iron without prior separation stages other than removal of the graphitic carbon. Selectivity was achieved without the use of complexing agents or close control of pH.

In their work on chromatographic separations, Cerrai and Testa[2,43,44] and Pierce *et al.*[47,48,49] have demonstrated that the often difficult separation of rare earth mixtures can be achieved quite readily using paper cellulose treated with liquid ion exchangers, while Damodaran,[54] Clifford and Irving[55] and Handley[42] have shown that the field of liquid ion exchange separations may become very much wider.

In radiochemical analysis, the fact that the activity of the organic phase may be measured directly shows a distinct advantage over the use of resin exchangers, where the particular isotopes have first to be eluted, then their activity measured.

Zusammenfassung—Eine Übersicht über neuere Anwendungen flüssiger Ionenaustauscher in der anorganischen Analyse wird vorgelegt.

Résumé—On présente une rèvue sur les emplois récents des échangeurs d'ions liquides en analyse inorganique.

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DETERMINATION OF LOW CONCENTRATIONS OF ACETALDEHYDE IN ETHYLENE OXIDE

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Summary—The method is based on a qualitative test for acetaldehyde in which the reagents sodium nitroprusside and piperidine react with acetaldehyde to form a coloured substance that can be determined photometrically. This substance is unstable, however, and after reaching a maximum value in about 25 sec the absorbance decreases. Ethylene oxide also reacts with sodium nitroprusside to form brownish substances, but this reaction is slower, the colour not developing for 100–120 sec. If, therefore, the absorbance is measured about 25 sec after adding the reagents, any disturbance from the ethylene oxide is avoided.

INTRODUCTION

THE determination of impurities in ethylene oxide is complicated by its low boiling point and by its reactivity with a large number of substances, there being few reagents that do not produce disturbing side reactions. Gas chromatography and direct spectrophotometry can be applied for acetaldehyde concentrations down to about 20 μmole/ml, but it is necessary to be able to determine concentrations as low as 0.2 μmole/ml. The following photometric method has been worked out for this purpose.

PRINCIPLES

Sodium nitroprusside reacts with a number of substances to form coloured compounds. It also reacts with an aqueous solution of acetaldehyde in the presence of an organic base such as piperidine.[1,2] The mechanism of the reaction of sodium nitroprusside with acetaldehyde has been discussed by Williams.[3] The reaction was described for the first time by Simon,[4] and its use has since been reported in several papers.[5–9] The base used was piperazine. The reaction has been used as a qualitative test for acetaldehyde in water.[4] The resulting colour, which is bluish-red, attains its maximum intensity after 20–30 sec, and then quickly decreases, to be replaced after about 1 min by the same golden brown colour as is obtained from a blank. A method based on the sodium nitroprusside reaction with an aqueous solution of acetaldehyde has recently been published.[10]

When added to ethylene oxide, which reacts with amines, and consequently with piperidine, sodium nitroprusside and piperidine give a brownish colour after 100–120 sec. By mixing sample and reagents in the cell of a direct reading spectrophotometer the development of the colour may be followed. A maximum at 575 nm results from the reaction of acetaldehyde, and the absorbance reaches its highest value after about 25 sec and then decreases. After 90–120 sec the absorbance increases again, now because of the reaction of ethylene oxide with the reagents: the substances formed absorb all visible radiation strongly.

The procedure described below enables the absorbance maximum from the acetaldehyde reaction to be read off easily on the instrument. A calibration curve based on such readings obeys Beer's law, and gives a molar absorptivity of 2000–3500 litre.cm^{-1}.mole^{-1}, depending on the dilution of the sample. Experiments have shown that the logarithm of the absorbance is a linear function of the ethylene oxide concentration at a given acetaldehyde concentration, and that the absorbance increases with a decreasing ethylene oxide concentration. This means that a nomogram can be constructed in such a way that only one calibration curve is necessary to cover any dilution of the sample.

The reaction may be disturbed by a number of substances (*e.g.*, organic sulphides and mercaptans) but not by the impurities normally present in ethylene oxide made from ethanol or ethylene. Formaldehyde does not interfere with the reaction, because only aldehydes capable of forming aldoles, *i.e.*, compounds with at least two carbon atoms, react with sodium nitroprusside.[3]

EXPERIMENTAL

Reagents

Piperidine: Puriss.

Sodium nitroprusside: In aqueous solution, 10% w/w; dissolve 10 g of $Na_2[Fe(CN)_5NO]2H_2O$ in 90 ml of distilled water.

Apparatus

Beckman B spectrophotometer: Setting: wavelength, 575 nm; photomultiplier, position A; sensitivity, 2; slit width, *ca.* 0·11–0·12 mm.

Standard solutions

A calibration curve has to be drawn for a suitable dilution of freshly distilled ethylene oxide with distilled water. Two dilutions of the ethylene oxide samples may be used, one of 5% v/v (dilution A) for concentrations of acetaldehyde in the sample exceeding $2{\cdot}3 \times 10^{-6}$ mole/ml (0·01% w/v), and one of 20% v/v (dilution B) for lower concentrations. At room temperature it is difficult to obtain good results with samples of a higher ethylene oxide concentration than 20% because of the low boiling point of ethylene oxide.

If the dilutions A and B are chosen, prepare two series of standard solutions as follows: make stock solutions of dilutions A and B, each containing 0·005% of acetaldehyde w/v. Transfer known volumes of the stock solution to volumetric flasks, and make up to the mark to give the appropriate dilution A or B. Prepare at least 4 solutions in each series, with the acetaldehyde concentrations evenly distributed over the range of measurement.

Blanks

Prepare blanks for the adjustment of the instrument as follows (three blanks are recommended to ensure reliable adjustment): pipette 0·30 ml of sodium nitroprusside solution into a 1-cm cell. (Experiments, in which the volume of nitroprusside solution was varied from 0·1 to 0·4 ml, indicated that the optimum volume was 0·3 ml.) Pipette 2·00 ml of dilution A or B (without acetaldehyde) and 0·20 ml of piperidine into a 5-ml test-tube, and shake carefully for 10–15 sec to obtain a homogeneous mixture. To avoid the formation of bubbles do not invert the test-tube when mixing, but effect the mixing by small rapid lateral movements of the tube. Nor should the mixture be shaken too long, (at most 10–15 sec), because the heat of reaction may produce vapour bubbles. After shaking, transfer the solution to the cell by means of a pipette. To ensure complete mixing in the cell use a 2-ml pipette provided with a rubber bulb, or use a syringe. To avoid the formation of bubbles, direct the solution along the wall of the cell. Within the next 25 sec set the absorbance scale of the spectrophotometer at zero with the slit, because after this time the solution may turn brown. Repeat the procedure for 3 blanks. Only 1 zero adjustment is necessary for each test series.

Calibration curve

Treat the prepared standard solutions as described above under *Blanks*. Pipette 0·30 ml of sodium nitroprusside solution into a 1-cm cell. Pipette 0·20 ml of piperidine and 2·00 ml of the standard solution into a 5-ml test-tube, mix, and transfer the mixture to the cell. Perform the measurement at once and at room temperature. After the sample and reagents are mixed the absorbance increases to reach a maximum after *ca.* 25 sec: this lasts a few seconds, after which the absorbance decreases again. Read off the maximum value, and use this for drawing the calibration curve.

Dilution A gives a linear calibration curve in the concentration range of $0 - 2 \times 10^{-6}$ mole of acetaldehyde per ml of undiluted ethylene oxide ($0 - 9 \times 10^{-3}\%$ w/v; absorbance 0–0·6) and dilution B gives a linear curve in the range of $0 - 4{\cdot}5 \times 10^{-6}$ mole of acetaldehyde per ml of undiluted ethylene oxide ($0 - 20 \times 10^{-3}\%$ w/v; absorbance 0–0·6).

Measurements of samples

Dilute the unknown ethylene oxide sample with distilled water to 5% (dilution A) or 20% (dilution B), the dilution depending on the expected concentration of acetaldehyde. Set the spectrophotometer at zero as described under *Blanks*. Perform the measurements as described under *Calibration curve*, with the standard solution replaced by 2·00 ml of the diluted sample solution. As mentioned under *Principles*, there is a linear relationship between the logarithm of the absorbance and the degree of dilution of the ethylene oxide sample. Therefore a nomogram can be constructed where the calibration curve for a chosen dilution of ethylene oxide can be used for any dilution of the sample.

DISCUSSION

To obtain good results the determinations must be made with great care. Routine measurements have, however, been carried out at our laboratory for more than a year without difficulties.

The standard deviations are $1{\cdot}5 \times 10^{-8}$ and $2{\cdot}4 \times 10^{-8}$ mole per ml of ethylene oxide (original sample) for dilutions of 5 and 20 times, respectively, of the sample. Because the accuracy of the final results is dependent on the purity of the ethylene oxide used for making the calibration curve, it is important that this should be freshly and carefully distilled. We have used a Podbielniak column (120 theoretical plates) for the distillation.

The method is applicable to ethylene oxide samples diluted at least 4:1; otherwise bubbles appear which make it impossible to measure the samples in a spectrophotometer at room temperature. Large amounts of propionaldehyde or acrolein ($>0{\cdot}1\%$) react with the sodium nitroprusside to increase the absorbance. The presence of formaldehyde does not affect the determination.

In most of the experiments piperazine has been used as the base. Lewin[1] describes experiments in which piperidine was used. A comparison between piperidine and piperazine that we carried out on samples with different concentrations of acetaldehyde showed that piperidine gives a 10 times higher absorptivity.

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Zusammenfassung—Bei einer qualitativen Probe auf Acetaldehyd reagiert dieser mit Nitroprussidnatrium und Piperidin zu einer photometrisch bestimmbaren farbigen Substanz. Die Substanz ist jedoch instabil; die Extinktion sinkt von einem nach etwa 25 Sekunden erreichten Maximalwert wieder ab. Äthylenoxyd readiert auch mit Nitroprussidnatrium zu bräunlichen Produkten; diese Reaktion ist langsamer, die Farbe tritt erst nach 100–120-Sekunden auf. Wird daher die Extinktion etwa 25 Sekunden nach Zugabe der Reagentien gemessen, so wird die Störung durch Äthylenoxyd vermieden.

Résumé—La méthode est basée sur un essai qualitatif de l'acétaldéhyde dans lequel le réactif: nitroprussiate de sodium et pipéridine, réagit avec l'acétaldéhyde pour donner une substance colorée, qui peut être dosée photométriquement. Cette substance est toutefois instable, et après avoir atteint une valeur maximale en 25 secondes environ, l'absorption décroît. L'oxyde d'éthylène réagit aussi avec le nitroprussiate de sodium pour former des substances brunâtres, mais cette réaction est plus lente, la couleur ne se développant pas pendant 100–120 secondes. Si, par conséquent, l'absorption est mesurée environ 25 secondes après l'addition des réactifs, toute perturbation dûe à l'oxyde d'éthylène est évitée.

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SEPARATION OF BISMUTH FROM LEAD, COPPER AND OTHER ELEMENTS BY MEANS OF ANION EXCHANGE

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Summary—The anion-exchange behaviour of bismuth and various other elements has been investigated in media consisting of methyl glycol and nitric acid. Through the determination of the distribution coefficients in such mixtures, a method for the anion-exchange separation of bismuth from many metal ions has been developed. A mixture of 90% methyl glycol and 10% 5*M* nitric acid is a suitable medium for this separation on the strongly-basic anion exchanger Dowex 1, X8. Only bismuth, thorium and lanthanum are strongly retained on the resin in these conditions. All other elements investigated, such as lead, copper, iron, *etc.*, are either only weakly adsorbed or are not absorbed. By means of this ion-exchange procedure, a series of analyses of copper-base alloys for bismuth has been carried out. The results show that this method can be used successfully for the quantitative isolation of bismuth from such materials. The final determination of bismuth in the eluates is performed by complexometric titration.

INTRODUCTION

THE anion-exchange behaviour of bismuth in pure aqueous nitric acid solutions has been investigated in detail by Buchanan and Faris,[1] who found that this element is rather weakly adsorbed on strongly basic anion-exchange resins, even at high concentrations of nitric acid; its adsorption is, however, markedly enhanced in the presence of ammonium nitrate. A similar increase has also been observed by Korkisch and Tera[2] in a 90% methanol–10% 5*M* nitric acid system, and Fritz and Greene[3] noted a similar phenomenon when they determined the distribution of bismuth in 1·5*M* nitric acid–85% isopropanol.

Because the adsorption of lead is comparatively high in both these organic solvent-nitric acid media, and also in 90% acetic acid–10% 5*M* nitric acid, as shown by Korkisch and Arrhenius,[4] a separation of these two elements from each other cannot easily be effected. Recent investigations by Korkisch and Feik[5] have shown that in a mixture consisting of 90% tetrahydrofuran and 10% 5*M* nitric acid the adsorption behaviour of bismuth and lead is such that a separation of these two elements can easily be carried out. Because bismuth is, however, accompanied by practically all other elements, its separation from metal ions such as copper, iron, nickel, zinc, *etc.*, is not feasible, and therefore a determination of bismuth in presence of all these elements is complicated by interferences. In order to overcome these difficulties several organic solvent-nitric acid mixtures have been studied. As a result of these investigations a medium consisting of methyl glycol and nitric acid has been found to be most suitable, not only for the separation of bismuth from lead, but also from practically all other elements usually present in copper-base alloys. The method described here can therefore be applied to the isolation and determination of bismuth in such alloys.

Because uranium can also easily be separated from bismuth, which is used in reactor cooling systems, this method might prove of importance in the field of reactor chemistry.

EXPERIMENTAL

Reagents

Ion-exchange resin: The strongly-basic anion exchanger Dowex 1, X8 (100–200 mesh, nitrate form) was used.

Standard solutions of bismuth and other elements: Solutions in 5*M* nitric acid, of precisely known element content, were employed.

Organic solvent: Methyl glycol of reagent-grade purity.

Wash solution: 90% (vol) of methyl glycol + 10% (vol) of 5*M* nitric acid.

Apparatus

The column operations were carried out in columns of the type and dimensions described earlier.[6] The height of the resin bed was 10 cm and its diameter 0·6 cm.

Quantitative determination of elements investigated

The determinations of bismuth and all other elements except uranium, which was determined fluorimetrically,[7] were performed by titration with 0·01*M* or 0·001*M* EDTA, using suitable indicators, *e.g.*, Xylenol Orange.

Determination of distribution coefficients

The distribution coefficients of all elements were determined in the manner described earlier.[8]

Column operations

All separations on resin columns were performed by the following working procedure.

Pretreatment of resin bed: Before passage of the sorption solution the resin was treated with 50 ml of the wash solution.

Sorption step: The sorption solution was prepared by diluting 2 ml of 5*M* nitric acid, containing the metal ions in question, with methyl glycol to 20 ml. This solution was passed through the column at a flow rate of 0·5 ml/min. During this operation, bismuth, thorium and lanthanum were strongly adsorbed, and lead to some extent; the other elements, such as copper, zinc, *etc.*, passed into the effluent.

Washing step: To remove lead completely from the column the resin bed was washed with 150 ml of the wash solution used in small portions.

Elution: The bismuth was eluted with 100 ml of 1*M* nitric acid. After evaporation of the eluate, bismuth was determined by titration with EDTA using Xylenol Orange as indicator.

*In the analysis of copper-base alloys, 2 g of the sample were dissolved in nitric acid and the residue obtained after evaporation of the solution was dissolved in 10 ml of 5*M* nitric acid. To 1-ml aliquot of this solution 1 ml of a bismuth standard solution was added, and after dilution to 20 ml with methyl glycol the solution was passed through the column as described above. In blank runs, 1 ml of 5*M* nitric acid was used instead of the bismuth standard solution.

RESULTS

Investigation of the effect of methyl glycol concentration on the adsorption of bismuth at a constant over-all nitric acid concentration of 0·5*M* (10% of 5*M* nitric acid) showed a linear decrease of the distribution coefficient with decreasing concentration of organic solvent.

An increase of the nitric acid concentration in solutions consisting of 90% methyl glycol caused the distribution coefficient of bismuth to increase linearly from 115 (in the presence of 10% of 2·5*M* nitric acid) to 460 (in presence of 10% of 10*M* nitric acid). Although better adsorption can evidently be achieved in the latter case, mixtures with 10% of 5*M* nitric acid were invariably used for all other experiments, such as the separations, because the solubility of the nitrates of the investigated metal ions is still high enough in these media, whereas at much higher concentrations of nitric acid the solubility is low.

Loading experiments showed that the distribution coefficient of bismuth decreases with increasing load from 230 to 185, when equilibrating 5–30 mg of bismuth with 1 g of the resin.

Investigation of the adsorption of various other elements in 90% methyl glycol–10% 5*M* nitric acid media showed that besides bismuth only lanthanum and thorium are strongly retained on the resin. The results of these experiments are recorded in Table I.

TABLE I.—DISTRIBUTION COEFFICIENTS IN 90% METHYL GLYCOL–10% 5*M* NITRIC ACID ON DOWEX 1, X8

Metal ion	Distribution coefficient, 5 mg/20-ml load
Bi^{III}	230·
Pb^{II}	28·6
Cu^{II}	<1·
Zn^{II}	<1·
Cd^{II}	5·
Al^{III}	<1·
Ga^{III}	2·2
In^{III}	7·7
Mn^{II}	<1·
Fe^{III}	<1·
Co^{II}	<1·
Ni^{II}	<1·
Zr^{IV}	<1·
Hf^{IV}	3·
Th^{IV}	1,700·
Mg^{II}	<1·
Ca^{II}	5·
Sc^{III}	<1·
La^{III}	9,000·
Yb^{III}	4·
UO_2^{II}	6·6

It is seen that bismuth can easily be separated from most of the elements listed in Table I. Fractions of micrograms of the element can be separated from milligram quantities of other metals. For the quantitative separation from lead, however, a prolonged treatment with the wash solution is necessary (see *Experimental*).

Based on all these investigations several samples of copper-base alloys to which known amounts of bismuth were added have been analysed using the working procedure described above. From the results of these experiments, which are shown in Table II, it is seen that in all cases a quantitative separation of bismuth from the elements present in the samples was achieved, the error being within small limits. From a number of experiments with varying amounts of the elements, a relative standard deviation of ±1·65% was calculated.

In order to demonstrate the effectiveness of the separation method more clearly, a typical separation of lead from bismuth is shown in Fig. 1 from which it is seen that even when washing with 260 ml of the wash solution no trace of bismuth appears in the effluent. Because practically all other elements investigated except lanthanum

TABLE II.—DETERMINATION OF BISMUTH IN COPPER-BASE ALLOYS

Composition of alloy (major constituents)	Bismuth added, *mg*	Bismuth found, *mg*
1. Cu (65%), Zn (35%)	0·0	0·0
	0·5	0·51
	5·0	5·02
	10·0	9·98
2. Cu (65%), Zn (16%)	0·0	0·01
Ni (17%), Pb (1%)	0.5	0·5
Fe (0·7%)	5·0	5·02
	10·0	10·03
3. Cu (70%), Zn (30%)	0·0	0·0
	0·5	0·48
	5·0	5·01
	10·0	10·0
4. Cu (80%), Zn (10%)	0·0	0·0
Pb (8%)	0·5	0·51
	5·0	4·98
	10·0	9·99
5. Cu (75%), Zn (10%)	0·0	0·02
Ni (5%), Pb (5%)	0·5	0·52
	5·0	5·03
	10·0	10·04

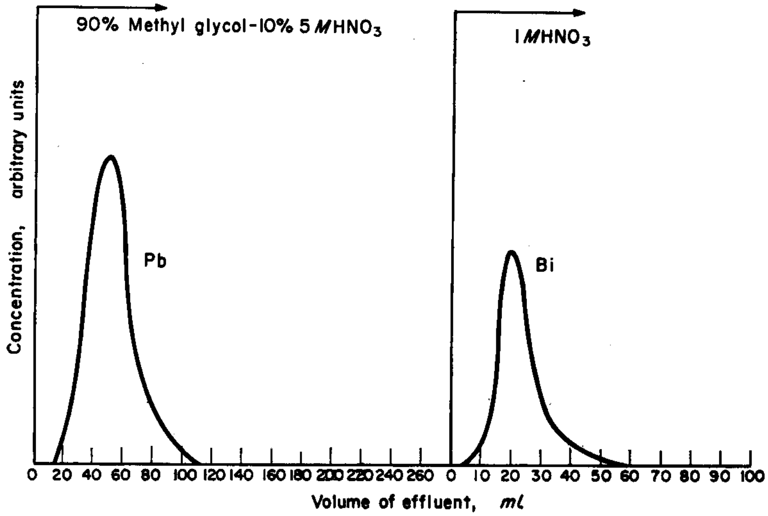

FIG. 1.—Separation of lead from bismuth.

and thorium have distribution values smaller than that of lead (see Table I), their quantitative separation from bismuth can effectively be carried out even if present in large amounts (see Table II).

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Zusammenfassung—Das Anionenaustauschverhalten von Wismuth und verschiedener anderer Elemente wurde in Medien bestehend aus Methyl-Glykol und Salpetersäure untersucht. Auf Grund von Bestimmungen der Verteilungskoeffizienten in solchen Mischungen wurde eine Methode zur Anionenaustauschtrennung des Wismuts von vielen Metallionen entwickelt. Eine Mischung bestehend aus 90% Methyl-Glycol und 10% 5*M* Salpetersäure erwies sich als am besten geeignet zur Trennung am stark basischen Anionenaustauscher Dowex 1, X8. Unter diesen Bedingungen werden nur Wismut, Thorium und Lanthan stark am Harz adsorbiert während alle anderen Elemente wie z.B. Blei, Kupfer, Eisen etc. überhaupt nicht oder nur schwach festgehalten werden. Mittels dieses Verfahrens wurde Wismut in einer Anzahl von Kupferlegierungen bestimmt. Die Ergebnisse dieser Untersuchungen zeigten, daß diese Methode erfolgreich zur quantitativen Abtrennung des Wismuts aus solchen Materialien angewendet werden kann. Die Endbestimmung des Wismuts in den Eluaten erfolgte durch komplexometrische Titration.

Résumé—On a étudié le comportement, au point de vue échange anionique, du bismuth et de divers autres éléments dans des milieux propylèneglycol-acide nitrique. Par la détermination des coefficients de distribution dans de tels mélanges, on a élaboré une méthode de séparation par échange anionique du bismuth de nombreux autres ions métalliques. Un mélange composé de 90% de propylèneglycol et 10% d'acide nitrique 5*M* s'est révélé être le milieu le plus convenable pour cette séparation, sur l'échangeur anionique fortement basique Dowex 1, X8. Seuls, le bismuth, le thorium et le lanthane sont fortement retenus sur la résine dans ces conditions, cependant que tous les autres éléments étudiés, tels le plomb, le cuivre, le fer, etc..., ne subissent qu'une adsorption faible ou nulle. Au moyen de cette méthode d'échange d'ions, on a effectué une série d'analyses, concernant le bismuth, sur des alliages à base de cuivre. Les résultats de ces recherches ont montré que cette méthode peut être utilisée avec succès pour l'isolement quantitatif du bismuth de tels matériaux. Le dosage final du bismuth dans les éluats a été effectué par titrage complexométrique.

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NUCLEATION OF LEAD CHROMATE FROM HOMOGENEOUS SOLUTION

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Summary—On the basis of the Christiansen-Nielsen model for nucleation, the nucleus of lead chromate precipitated from homogeneous solution has been found to consist of about five ions. The critical supersaturation values of solutions of lead chromate are dependent upon the method of filtration; however, a change in supersaturation of about 25% is without effect on the size of the critical nucleus.

THE nucleation of sparingly soluble salts may be considered to take place in two steps, the first being the production of supersaturation within the system and the second the formation of the nucleus within the supersaturated system.[1,2] In the present investigation an attempt is made to elucidate the mechanism of nucleation of lead chromate, to determine the degree of supersaturation which must be attained for nucleation to occur, and to learn the effect of the degree of supersaturation on the size of the critical nucleus.

Christiansen and Nielsen[3] proposed that the mechanism of nucleation proceeds by a series of bimolecular collisions between precipitating ions and subcritical embryos. Klein, Gordon and Walnut[4] modified the Christiansen-Nielsen approach to make it applicable to the determination of the critical nucleus size in precipitations from homogeneous solution. In their modification, they obtained

$$\mathrm{N} = \mathrm{k}\int[\mathrm{I.P.}]^{n}\,\mathrm{dt} \qquad (1)$$

where N = number of nuclei and hence number of particles found,
k = a constant,
I.P. = ion product,
n = nucleus size,
and t = time.

Thus, by determining N, the number of particles formed, and evaluating the variation of the ion product with time, one can determine n, a measure of the number of ions in the critical nucleus. Klein *et al.*[4] studied the precipitation of silver chloride from homogeneous solution and determined that the critical nucleus consisted of five ions.

The present investigation was undertaken to study the nucleation of lead chromate from homogeneous solution. The chromate ion was generated by the reaction[5] of chromium(III) with bromate in the presence of lead ion, the stoichiometry of the reaction being:

$$10\mathrm{Cr}^{3+} + 6\mathrm{BrO}_3^{-} + 22\mathrm{H}_2\mathrm{O} \rightarrow 10\mathrm{CrO}_4^{2-} + 3\mathrm{Br}_2 + 44\mathrm{H}^{+}.$$

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EXPERIMENTAL

Reagents

All stock solutions were prepared from reagent-grade chemicals. All solutions, except lead and chromium(III) nitrates, were prepared by weighing the dry reagent and diluting to volume. The necessary dilutions were made with distilled water previously filtered through a Millipore HA filter. There was no further standardisation of these solutions.

The stock solution of lead was standardised gravimetrically by precipitation of the sulphate. The chromium(III) solution was standardised by oxidation to chromate with sodium peroxydisulphate, followed by addition of a known amount of iron(II) sulphate and titration with standard potassium permanganate.[6]

Apparatus

Spectrophotometric measurements were performed with a Beckman DU spectrophotometer fitted with a dual thermospacer set, which permitted circulation of water around the cell housing compartment to maintain constant temperature in the cells. Fused 10-mm silica cells were used.

Turbidimetric measurements were made using a Phoenix-Brice light scattering instrument equipped with a thermostatted jacket which encircled a cylindrical cell; a 430-mμ filter was used.

Procedure

Appropriate amounts of stock solutions of lead nitrate, potassium bromate, potassium nitrate and equimolar acetic acid-sodium acetate buffer were drawn through a Millipore filter into a 500-ml volumetric flask; potassium nitrate was used to vary the ionic strength of the medium. The resulting solution was diluted to approximately 400 ml with pre-filtered distilled water. A solution of chromium(III) ions was then introduced into the reaction mixture through the Millipore filter and the contents were diluted to volume with water. The time was measured from the moment of addition of chromium(III) ions to the other reagents. Portions of the solution were transferred to optical cells for spectrophotometric and turbidimetric measurements and to Erlenmeyer flasks for later use in sampling studies. All reaction vessels were maintained at 25° ± 0·2°.

Spectrophotometric determination of chromate. The photometer was used to determine the concentrations of chromate ion in the solution up to the onset of precipitation. The wavelength used was 340 mμ, at which the molar extinction coefficient for chromate ion is $1{\cdot}51 \times 10^3$ cm^2.mole^{-1}. Because the precipitate particles acted as light scattering centres, thus introducing an uncertainty in the absorbance readings, it was necessary to extrapolate the absorbance-time curve in order to determine the total chromate ion produced.

Titrimetric determination of lead. To determine the amount of lead ion precipitated and therefore the concentration of lead ion remaining in solution, it was necessary to pipette 50-ml portions of the reacting solution and transfer these into 50-ml Erlenmeyer flasks suspended in the constant temperature bath. Then, approximately 40 min after the start of precipitation and every 20 min thereafter, one of the samples was filtered through a Millipore VC filter. The precipitate particles on the walls of the flask and on the filter were dissolved in concentrated potassium hydroxide, the solution transferred to a 100-ml volumetric flask and analysed for chromate; the amount of lead ion precipitated was determined from this measurement.

Turbidimetric determination of onset of precipitation. Turbidimetric measurements were made to determine the time at which precipitation began. The relative turbidity was plotted as a function of time and the inception of precipitation taken to be the time at which there was a sharp increase in the slope of the turbidity-time curve.

RESULTS AND DISCUSSION

Size of nucleus

The solution concentrations of lead and chromate ions were determined from the analytical results; a typical plot of the variation of the ion product ($[Pb^{2+}].[CrO_4^{2-}]$) with time is shown in Fig. 1. The lead concentration in solution was considered to be that remaining uncomplexed by acetate.[7] According to equation (1), when the variation of the ion product with time and the quantity of nuclei, *i.e.*, the particle count, is known, it is possible to determine the number of ions in the critical nucleus. (The particle count was determined microscopically.)

For each experiment, the *ion product* was plotted as a function of *time*. If the ion product, raised to a power x (selected integral values), is plotted *versus* time the area under the curve is the value $\int(\text{I.P.})^x\,dt$. If this value is divided by the particle count N, a value of $1/k$ is obtained. For each selected value of x, $1/k$ for each run was plotted *versus* $\int(\text{I.P.})^x\,dt$. Where $d(1/k)/d\int(\text{I.P.})^x\,dt$ *versus* x was zero, the term $1/k$ was taken as constant and x to be equal to n, where $2n - 1$ represents the number of ions in the critical nucleus. The limits for the integration of $(\text{I.P.})^x$ *versus* time were chosen to include essentially all ion products at which nucleation was occurring. For these experiments the limiting ion product chosen was $1{\cdot}70 \times 10^{-9}$ mole^2.l.$^{-2}$.

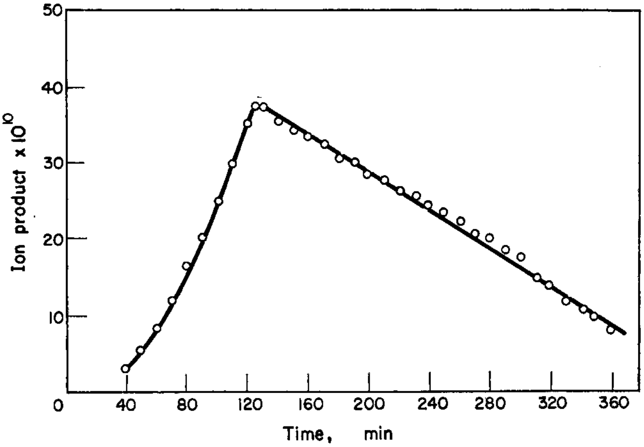

FIG. 1.—Ion product of lead chromate as a function of time during the precipitation.

Table I summarises the values used in the determination of the critical nucleus size. The results indicate n to be three; therefore, the number of ions in the critical nucleus is five.

TABLE I.—DETERMINATION OF THE SIZE OF THE NUCLEUS OF LEAD CHROMATE[a]

$[\text{Pb}^{2+}]$, *mole.l.*$^{-1}$ $\times 10^4$	Number of particles, N.*l.*$^{-1}$ $\times 10^{-7}$	$\frac{\int(I.P.)^1\,dt}{N} \times 10^{15}$	$\frac{\int(I.P.)^2\,dt}{N} \times 10^{23}$	$\frac{\int(I.P.)^3\,dt}{N} \times 10^{32}$	$\frac{\int(I.P.)^4\,dt}{N} \times 10^{40}$	$\frac{\int(I.P.)^5\,dt}{N} \times 10^{49}$
7·46	1·92	2·28	1·03	3·38	0·95	2·48
9·95	1·40	0·29	1·32	4·36	2·43	3·12
14·9	8·78	3·12	0·13	0·38	0·11	0·30
19·9	4·53	0·61	0·26	0·78	0·23	0·72
29·9	1·44	2·94	1·74	6·26	2·07	9·03
Slope of plot of $\frac{\int(I.P)^n\,dt}{N}$ *vs.* $\int(I.P.)^n\,dt$		$1{\cdot}06 \times 10^{-7}$	$1{\cdot}20 \times 10^{-7}$	$6{\cdot}82 \times 10^{-7}$	$0{\cdot}94 \times 10^{-7}$	$0{\cdot}82 \times 10^{-7}$

[a] Millipore HA filter used.

The values presented in Table I are for experiments conducted with Millipore HA filters (pore size = 0·45 μ). In order to determine whether the filtration process has any effect on the nucleus size, an analysis of the results from experiments using Millipore VC filters (pore size = 0·1 μ) was made. These results are shown in Table II. Again, n was found to be three, showing the number of ions in the critical nucleus to be independent of the filter pore size.

This part of the study demonstrates the use of kinetic methods to determine the size of the critical nucleus of lead chromate, thus supporting the model for nucleation proposed by Christiansen and Nielsen. Although the critical nucleus of lead chromate consists of five ions, the significance of this number is its order of magnitude. Christiansen and Nielsen's induction time experiments, used to determine the nucleus size, have been criticised because the use of direct mixing of reactants may possibly cause nucleation to occur during the mixing process rather than having it occur after the system becomes homogeneous. The present work eliminates the effect of direct mixing by using the technique of precipitation from homogeneous solution, with, however, the results still in agreement with the model for nucleation as proposed by Christiansen and Nielsen.

TABLE II.—DETERMINATION OF THE SIZE OF THE NUCLEUS OF LEAD CHROMATE[a]

$[Pb^{2+}]$, *mole.l.*$^{-1}$ × 10^4	Number of particles, N.*l.*$^{-1}$ × 10^{-7}	$\frac{\int(I.P.)^1\,dt}{N}$ × 10^{15}	$\frac{\int(I.P.)^2\,dt}{N}$ × 10^{23}	$\frac{\int(I.P.)^3\,dt}{N}$ × 10^{32}	$\frac{\int(I.P.)^4\,dt}{N}$ × 10^{40}	$\frac{\int(I.P.)^5\,dt}{N}$ × 10^{48}
9·95	2·59	8·65	4·09	7·80	5·40	1·69
19·9	9·36	0·97	0·51	2·10	0·36	0·30
24·9	3·99	2·83	1·67	7·99	3·36	1·56
29·9	15·6	0·36	0·20	0·92	0·34	0·14
Slope of plot of $\frac{\int(I.P.)^n\,dt}{N}$ *vs* $\int(I.P.)^n\,dt$		$5·18 \times 10^{-8}$	$5·40 \times 10^{-8}$	$25·9 \times 10^{-8}$	$4·28 \times 10^{-8}$	$3·93 \times 10^{-8}$

[a] Millipore VC filter used.

Effect of supersaturation

This phase of the investigation involved a study of the effect of filtration, the rate of generation of the chromate ion and the variation of the ionic strength of the medium upon the supersaturation ratios which were reached before precipitation was first observed. The "critical"[*] supersaturation ratio, S_{crit}, is defined as $[(I.P.)/K_{sp}]^{1/2}$, where K_{sp} is the equilibrium solubility product. The turbidimetric measurements were used to determine the time of inception of precipitation. The concentration of chromate ion used for the ion product was taken from the absorbance-time curve and the lead ion concentration was taken as the uncomplexed ion initially present.

Effect of filtration on S_{crit}. Two filters of different pore size were used in the preparation of the reacting solutions; these were Millipore HA filters with a nominal pore size of 0·45 μ and Millipore VC filters with a nominal pore size of 0·1 μ. The results of these experiments are shown in Table III, S_{crit} being calculated on the basis of concentration. The supersaturation ratios varied inversely with the pore size of the filter. With the HA filter, S_{crit} is 104 ± 3; with the VC filter, it is 128 ± 8, *i.e.*, a 25% change for the four-fold variation in filter pore size.

If nucleation occurs by a heterogeneous process involving a foreign body, then the finer filter must remove some of the larger (or more active) nucleation sites so that the

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[*] A purely critical value does not exist (*cf.* Nielsen[13]). It appears to be critical only because the rate of formation of nuclei changes drastically with supersaturation. As a result, the experimental range, within which the rate of nuclei formation can be followed, is quite restricted.

system can become more supersaturated before nucleation occurs. Thus the first step in the nucleation mechanism, rather than being a reaction between the two ions comprising the precipitate, is a "reaction" between either one or other of their ions (or both) and a foreign site M, as follows:

$$M + Pb^{2+} = MPb^{2+}$$

or

$$M + CrO_4^{2-} = MCrO_4^{2-}$$

TABLE III.—EFFECT OF FILTRATION ON THE CRITICAL SUPERSATURATION RATIO OF LEAD CHROMATE

Filtration	$[Pb^{2+}]$, *mole.l.*$^{-1}$ × 10^4	S_{crit}
Millipore HA	7·46	102
Millipore HA	9·95	102
Millipore HA	14·9	100
Millipore HA	19·9	104
Millipore HA	29·9	110
Millipore VC	9·95	116
Millipore VC	19·9	124
Millipore VC	24·9	138
Millipore VC	29·9	136

Effect of rate of generation of chromate ion. The rate was altered by varying the concentration of chromium(III) and bromate ions in the reacting solutions. The results of these experiments are shown in Table IV; the times indicated are those at which precipitation was first detected turbidimetrically. It was noted, although the times varied considerably (45–157 min), that there was no change in S_{crit}. If the value of the supersaturation ratio were not critical, but merely dependent upon the time required for the system to reach a particular supersaturation,[8] one might expect that the value of the supersaturation ratio at which precipitation is first detected should change. This result was not observed for the nucleation of lead chromate. Thus, the supersaturation ratio is truly "critical" at least for the particular set of experimental conditions utilised here.

TABLE IV.—EFFECT OF THE RATE OF GENERATION OF CHROMATE ION ON THE CRITICAL SUPERSATURATION RATIO OF LEAD CHROMATE

$[Pb^{2+}]$, *mole. l.*$^{-1}$ × 10^4	$[Cr^{+3}]$, *mole. l.*$^{-1}$ × 10^3	$[BrO_3^-]$, *mole. l.*$^{-1}$ × 10^3	S_{crit}	Time, *min*
9·95	3·77	4·00	118	157
19·9	3·77	4·00	100	89
9·95	4·71	5·00	102	128
19·9	4·71	5·00	104	84
9·95	5·65	6·00	104	75
19·9	5·65	6·00	109	45

Effect of ionic strength of reacting solution. The ionic strength was varied by adding known quantities of potassium nitrate; the mean activity coefficient for lead chromate was calculated from the Debye-Hückel equation. The results of these experiments are shown in Table V. The critical supersaturations show no apparent variation with change in ionic environment. This is a surprising result, for if the mechanism for nucleation involves an ionic dependence, then a large concentration of foreign ions would decrease the electrostatic attraction between the ions which can form the precipitate. Possible explanations for the results obtained are either (1) that the range over which the ionic strength was varied was insufficient or (2) that these experiments were conducted above a limiting value of the ionic strength. If the latter were the case, any further increase in the ionic strength would be without effect upon nucleation. Further, the values used for the mean activity coefficient for lead chromate may be inaccurate; LaMer and Dinegar[10] comment in a similar manner in their study of the precipitation of barium sulphate.

TABLE V.—EFFECT OF IONIC STRENGTH ON THE CRITICAL SUPERSATURATION RATIO OF LEAD CHROMATE

Method of filtration	Ionic strength, $\mu \times 10^2$	Mean activity coefficient, f	S_{crit}[a]	S_{crit}[b]
Millipore HA	8·5	0·356	100	35·6
	8·5	0·356	102	36·3
	8·5	0·356	102	36·3
	8·5	0·356	104	37·0
	8·5	0·356	110	39·2
	9·8	0·337	114	38·4
	10·5	0·328	117	38·4
	10·5	0·328	120	39·3
	11·0	0·321	116	37·2
	13·5	0·294	136	40·0
	13·7	0·292	113	33·0
	18·5	0·256	118	32·3
				(ave.) 37 ± 2
Millipore VC	8·5	0·356	116	41·3
	8·5	0·356	124	44·2
	8·5	0·356	132	47·0
	8·5	0·356	138	49·1
				(ave.) 45 ± 3

[a] Calculated from concentrations.
[b] Calculated from activities.

Relation between nucleus size and supersaturation

It is informative to examine the relationship between supersaturation and nucleus size according to the Ostwald-Freundlich equation:[11]

$$r = \frac{2\sigma M}{RT\rho \ln S}$$

where r = radius of the nucleus,
σ = interfacial tension,
M = molecular weight,
ρ = density,
S = supersaturation,
and R and T have their usual meanings.

When this equation is used to calculate the size of the nucleus of lead chromate, using values of 40 for the supersaturation and of 150 dynes/cm² for the interfacial tension,[11] the radius is found to be 40 Å. This radius is considerably greater than that of the Christiansen-Nielsen model, for which the rather small nucleus size of five ions is found. Furthermore, there is no interdependence of nucleus size and supersaturation as with the Ostwald-Freundlich equation. A homogeneous 40-Å radius nucleus would contain hundreds of ions. It seems improbable that a nucleus of such size could be built up either by a kinetic process or by concentration fluctuations. One possibility is that the bulk of such a nucleus might consist of a heterogeneous site (solvent or foreign impurity) with the ions contributing little volume to its actual size. Thus, it has been suggested that the Ostwald-Freundlich nucleus consists of the ions and the foreign site while the Christiansen-Nielsen nucleus is the ion aggregate only.[12]

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Zusammenfassung—Auf Grund des Keimbildungsmodells von Christiansen-Nielsen wurde gefunden, daß der Keim für die Fällung von Bleichromat aus homogener Lösung aus etwa 5 Ionen besteht. Die Werte für die kritische Übersättigung von Bleichromatlösungen hingen von der Filtrationsmethode ab; eine Änderung der Übersättigung um etwa 25% wirkte sich aber auf die Größe des kritischen Keimes nicht aus.

Résumé—Sur la base dur modèle Christiansen-Nielsen pour l'amorçage on a trouvé que le germe de chromate de plomb précipité d'une solution homogène est constitué par environ cinq ions. Les valeurs critiques de sursaturation des solutions de chromate de plomb dépendent de la méthode de filtration; toutefois, un changement d'environ 25% dans la sursaturation est sans effet sur la dimension du germe critique.

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SEPARATION AND DETERMINATION OF TANTALUM AND NIOBIUM BY PRECIPITATION FROM HOMOGENEOUS SOLUTION*

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Summary—An attempt to separate niobium and tantalum by precipitation from homogeneous solution by thermal decomposition of their peroxy complexes, in the presence of tannin and oxalate, has been only moderately successful. A more satisfactory separation of tantalum and niobium for ratios from 50:1 to 1:30 is obtained by extracting the bisulphate melt with ammonium oxalate before adding hydrogen peroxide, hydrochloric acid and tannin. For a tantalum/niobium ratio of 1:1 the niobium coprecipitation is reduced to 5%. Furthermore, two alternative possibilities are presented: (1) a quantitative recovery of a tantalum precipitate at small oxalate and high tannin concentration, leaving 90% of the tantalum-free niobium in solution; (2) an 85% recovery of niobium-free tantalum at high oxalate and small tannin concentration. A study of the coprecipitation process of niobium shows that the distribution coefficients follow a logarithmic pattern, true homogeneous mixed crystals being formed.

INTRODUCTION

BECAUSE of the similarity of their chemical properties, the gravimetric separation of tantalum and niobium from each other has always presented a very difficult problem in analytical chemistry. Probably the most reliable, but tedious, procedure for the separation is a fractional tannin precipitation. This procedure, developed by Powell and Schoeller,[1] is based on the difference in the stability of the oxalato-complexes. Precipitation from homogeneous solution was recently proposed by the present authors for the separation and determination of tungsten,[2] titanium, tantalum and niobium,[3] based on the thermal decomposition of soluble peroxy complexes from a hydrogen peroxide medium. An analogous procedure can readily be adapted for the separation and determination of niobium and tantalum. Radioactive tracer techniques were used to develop the proposed method.

EXPERIMENTAL

Radioisotopes

Tantalum. ^{182}Ta, β,γ-emitter, half-life ± 111 days, produced by irradiation of Ta_2O_5 in the BR-1 reactor.

Niobium. ^{95}Nb, β,γ-emitter, half-life ± 35·5 days, obtained from the Radiochemical Centre, Amersham, England.

Counting techniques. Integral γ-counting was performed for ^{182}Ta and ^{95}Nb using a standard scintillation counter with a well-type sodium iodide (thallium activated) crystal. In the presence of each other they were measured by differential γ-counting, using a 3″ × 3″ sodium iodide (thallium activated) crystal connected to a 400-channel analyser.

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Procedure

Precipitation of tantalum. Fuse the mixture of the oxides with potassium bisulphate and remove the cold melt from the crucible by warming with 5% ammonium oxalate. Rinse the contents of the crucible into a beaker and heat with water until a clear solution is obtained. Add 2 ml of 30% hydrogen peroxide, an adequate amount of 12*M* hydrochloric acid and an amount of tannin corresponding to 20 times the weight of the acids. Dilute the solution with water to obtain a final concentration of earth acid oxides of 0·02%, an ammonium oxalate concentration of 1% and an acidity of 2·5*M* hydrochloric acid. Decompose the peroxides by heating at 85° for 7–8 hr, and collect the dense precipitate. Some results are summarised in Table III.

Precipitation of niobium. Evaporate the filtrate from the tantalum precipitation to about 200 ml, and add 5–10 ml of nitric acid (sp. gr. 1·4) to clarify the dark-coloured solution. Oxidise the excess of oxalate with an adequate amount of sodium bromate, added dropwise. Neutralise with aqueous ammonia and precipitate the niobium with a ten-fold excess of tannin. Heat the solution to boiling over 5 min.

Precipitation of Tantalum from Homogeneous Solution

Tantalum is incompletely precipitated (95%) by the thermal decomposition of soluble peroxy-tantalate and -niobate in a homogeneous ammonia-hydrogen peroxide solution at pH 10 or 11; niobium is coprecipitated (at least 40%). Thermal decomposition of peroxytantalate in an acetate, citrate or tartrate solution, in the presence of tannin, results in an incomplete and voluminous precipitation. In an acid oxalate-tannin solution, however, a dense and readily filterable precipitate was obtained. Preliminary experiments showed that optimum results were obtained in an acidic medium (5*M* nitric acid); recoveries of 99·8% were achieved.

Separation of tantalum and niobium

In the present case, γ-spectrometric measurements offer a relatively simple means of determining the amounts of coprecipitated niobium as a function of the amount of precipitated tantalum. The gamma rays at 1·12, 1·15, 1·19, 1·22 and 1·23 *MeV* of ^{182}Ta can be measured independently from the activity of ^{95}Nb. The ^{95}Nb content can be computed from the activity under the 0·776 *MeV* peak, after subtraction of the Compton continuum of ^{182}Ta. For ^{182}Ta, the ratio of the activity under the peaks at about 1·2 *MeV* to the activity in the energy range about 0·776 *MeV* is, under standard conditions, a constant.

It appears that for the precipitation of tantalum from the homogeneous peroxide solution, optimum results are obtained in the presence of 1200 mg of oxalic acid, together with tannin and selenous acid. The respective amounts of the latter should correspond to 7 and 0·5 times the weight of the pentoxides. Different amounts of tantalum were precipitated from 200 ml of solution. The results are given in Table I.

TABLE I.—PRECIPITATION OF THE EARTH ACIDS AS A FUNCTION OF THEIR CONCENTRATION

Taken, *mg*		Heating period, *hr*	Ta left in solution, %	Nb coprecipitated, %
Ta_2O_5	Nb_2O_5			
20·0	20·0	24	0·6	10·5
50·1	50·0	10	0·9	19
75·2	75·1	5	1·3	34

From Table I it appears that from the most dilute solution 99·4% of the tantalum was recovered, the niobium coprecipitation being reduced to 10·5%.

A decrease of the coprecipitation was observed by extracting the bisulphate melt of 20 mg of tantalum pentoxide and 20 mg of niobium pentoxide with ammonium oxalate before adding the hydrogen peroxide. The precipitations were also carried out in the presence of different amounts of nitric, hydrochloric and selenous acids, ammonium oxalate and tannin, the volume of the solution being 200 ml.

Typical results are given in Table II.

TABLE II.—SEPARATION OF THE EARTH ACIDS IN THE PRESENCE OF AMMONIUM OXALATE

$(NH_4)_2Ox$, %	Acid	Ratio to the oxides (w/w) H_2SeO_3	Ratio to the oxides (w/w) Tannin	Heating period, *hr*	Ta left in solution, %	Nb coprecipitated, %
1	4·5*M* HNO_3	1	10	20	1·5	7·2
1	3*M* HNO_3	1	10	10	4·9	6·4
1	1·5*M* HCl	1	10	10	26·5	1·1
1	2·5*M* HCl	1	10	20	3·3	2·7
1	3·5*M* HCl	1	25	12	5·1	2·9
1	2·5*M* HCl	0	25	7	0·3	8·4
0·75	2·5*M* HCl	0	25	7	1·7	7·0
0·50	2·5*M* HCl	0	25	12	0·5	12·5
0·50	2·5*M* HCl	2	25	14	0·1	11·5
1·25	2*M* HCl	0	7	7	15·0	<0·5

From Table II it appears that, from a 0·5% ammonium oxalate solution and in the presence of a large amount of selenous acid, tantalum can be precipitated homogeneously with recoveries of 99·9%. From the γ-ray spectrum of the solution before and after precipitation, it is clear that the ^{182}Ta activity in the filtrate is undetectable. The last result given in Table II shows that it is possible to precipitate 85% of practically niobium-free tantalum. In the γ-ray spectrum of the precipitate, the niobium-peak at 0·776 *MeV* can barely be seen, although in the original solution it was as important as in the standard. These precipitations are interesting for preparative purposes. For a rapid analysis, however, optimum results were obtained by following the procedure, as shown in Table III.

TABLE III.—PRECIPITATION OF TANTALUM FROM HYDROGEN PEROXIDE OXALATE SOLUTION

Ta_2O_5 taken, *mg*	Ta left in solution, %
140·1	0·60
109·8	0·49
79·9	0·71
57·3	0·64
42·1	0·65
33·4	0·81
20·7	0·87
16·6	1·5^3
10·0	1·9^0
8·0	2·1^8

From Table III it appears that precipitation of tantalum from a homogeneous hydrogen peroxide-oxalate solution gives satisfactory tantalum recoveries.

Coprecipitation of niobium

The coprecipitation of niobium was investigated for niobium/tantalum ratios varying from 2 × 10^{-2} to 30. The absolute amount of tantalum precipitated varied from 100 mg for small ratios to 5 mg for larger ratios. The results are given in Fig. 1.

From Fig. 1 it appears that for a Nb_2O_5/Ta_2O_5 ratio equal to one the error on the tantalum determination is 5·5 %. If the precipitation is repeated, the error is reduced to 1 %. A correction can be made after a single precipitation if this ratio is higher than unity.

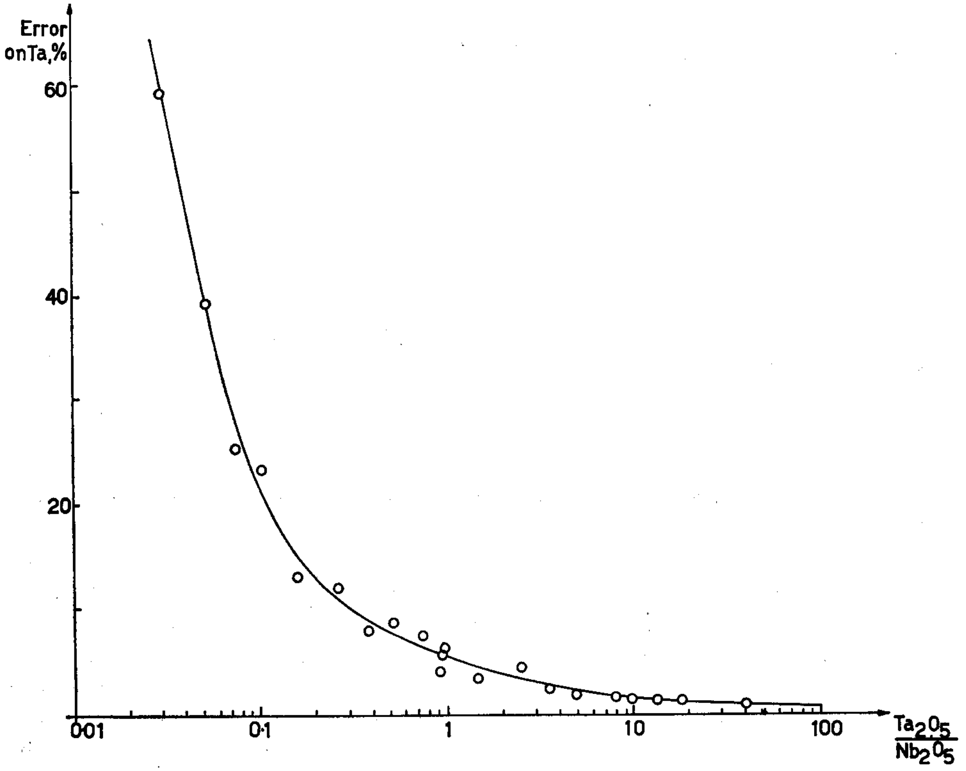

Fig. 1.—Coprecipitation of niobium with tantalum.

Precipitation of niobium from the filtrate after precipitation of tantalum

The amount of niobium left in solution was computed by adding, before the fusion, an adequate amount of ^{95}Nb of known activity (*ca.* 1 × 10^6 cpm) and counting an aliquot of the filtrate. The results are summarised in Table IV. It appears that this precipitation gives highly satisfactory niobium recoveries. The small amounts of tantalum and titanium present are coprecipitated quantitatively.

Determination of Distribution Coefficient

A coprecipitant can be distributed between solid and liquid phase according to an homogeneous,[4] logarithmic[5] or proportional distribution law.[6] As was shown in previous papers,[2,3] the coprecipitation process of molybdenum and vanadium with tungstic acid and of tungsten with the earth acids follows a linear pattern. In the present case, measurements of the radioactive isotopes offer a relatively simple means of determining the amount of coprecipitant as a function of the amount of precipitated carrier. To effect this, a small quantity of solution was removed at regular time intervals. The amount of each element present was then computed by γ-ray spectrometric analysis.

TABLE IV.—PRECIPITATION OF NIOBIUM IN THE FILTRATE

Taken, *mg*		Nb left in solution, %
Ta_2O_5	Nb_2O_5	
19·7	100·4	0·05
20·6	80·0	0·10
20·5	60·3	0·09
20·2	40·1	0·13
20·7	20·8	0·13
20·5	10·6	0·07
40·5	10·4	0·12
60·1	10·1	0·14
80·2	10·2	0·07

Procedure

Extract with 50 ml of 5% ammonium oxalate after bisulphate fusion of 43·8 mg of tantalum, and 5·6 mg of niobium, labelled with ^{182}Ta and ^{95}Nb, and transfer to a 400-ml conical flask fitted with a reflux condenser. Add 2 ml of 30% hydrogen peroxide, 50 ml of 12*M* hydrochloric acid and 1·5 g of tannin. Make the volume up to 300 ml. The activities of the tracer solutions are chosen to correspond respectively to *ca.* 3×10^6 and 5×10^6 cpm of ^{182}Ta and ^{95}Nb. Heat the solution for 7 hr at 85° and remove 5-ml portions by reverse filtration through an asbestos filter. Count 4-ml portions of these filtrates in standard vials with a multichannel analyser. The values of D, λ and K, corresponding to the different distribution constants, are presented in Table V.

From Table V it appears that the logarithmic distribution law is followed, the mean value being $\lambda = 0·030_4 \pm 0·001_3$.

TABLE V.—COPRECIPITATION OF NIOBIUM WITH TANTALUM

Ta pptd., %	Nb copptd., %	Distribution coefficients		
		D	λ	K
$42·5_1$	$1·7_4$	$0·023_9$	$0·031_8$	$0·040_9$
$72·6_3$	$4·3_8$	$0·017_4$	$0·034_6$	$0·060_3$
$83·7_8$	$6·3_6$	$0·013_1$	$0·036_1$	$0·075_9$
96·38	$9·9_7$	$0·0041_6$	$0·031_6$	$0·10_3$
97·56	$10·4_9$	$0·0029_3$	$0·029_8$	$0·10_7$
$98·82_5$	$11·3_6$	$0·0015_2$	$0·027_1$	$0·11_5$
$99·17_6$	$11·6_7$	$0·0011_0$	$0·025_8$	$0·11_8$
$99·25_9$	$12·2_3$	$0·0010_4$	$0·026_5$	$0·12_3$
			$\bar{\lambda} = 0·030_4 \pm 0·001_3$	

Furthermore, the experiments showed that the coprecipitation of niobium on tantalum also follows a logarithmic distribution if the bisulphate melt of the earth acids is extracted with hydrogen peroxide, the mean value of the distribution coefficient being $\lambda = 0·067 \pm 0·005$.

In this case, 61·5 mg of tantalum were precipitated in the presence of 5·25 mg of niobium. The concentration of oxalic acid was 1·5%; the solution contained 50 ml of 14*M* nitric acid and the precipitation was carried out with 0·75 g of tannin for a volume of *ca.* 200 ml. The results are presented in Table VI.

Table VI.—Coprecipitation of niobium with tantalum (melt extracted with hydrogen peroxide)

Ta pptd., %	Nb copptd., %	Distribution coefficients		
		D	λ	K
34·1	$2{\cdot}1_2$	$0{\cdot}041_9$	$0{\cdot}052_2$	0·062
65·1	$6{\cdot}5_0$	$0{\cdot}037_3$	$0{\cdot}063_4$	$0{\cdot}10_0$
84·5	$13{\cdot}8_0$	$0{\cdot}029_4$	$0{\cdot}079_6$	$0{\cdot}16_3$
87·6	$14{\cdot}8_1$	$0{\cdot}024_6$	$0{\cdot}077_1$	$0{\cdot}16_9$
95·94	$18{\cdot}2_4$	0·0094	$0{\cdot}062_8$	$0{\cdot}19_0$
			$\bar{\lambda} = 0{\cdot}067_0 \pm 0{\cdot}005_0$	

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Zusammenfassung—Einem Versuch zur Niob-Tantal-Trennung durch homogene Fällung in Gegenwart von Tannin und Oxalat durch thermische Zersetzung der Peroxykomplexe war nur mäßiger Erfolg beschieden. Eine bessere Tantal-Niob-Trennung in Verhältnissen von 50 : 1 bis 1 : 30 wurde jedoch erzielt durch Extraktion des Bisulfataufschlusses mit $(NH_4)_2Ox$ vor der Zugabe von H_2O_2, HCl und Tannin. Beim Niob-Tantal-Verhältnis 1 : 1 wird die Mitfällung von Niob auf 5% gedrückt. Darüber hinaus werden zwei Alternativen vorgeschlagen: 1) quantitative Tantalausbeute im Niederschlag bei kleiner Oxalat- und großer Tanninkonzentration, wobei 90% des Tantal-freien Niob in Lösung bleiben; 2) 85%-ige Ausbeute von Niob-freiem Tantal bei hoher Oxalat- und niedriger Tanninkonzentration. Die Verteilungskoeffizienten der Mitfällung von Niob verlaufen logarithmisch; es werden homogene wahre Mischkristalle gebildet.

Résumé—Un essai de séparation du niobium et du tantale par précipitation en milieu homogène en présence de tanin et d'oxalate, en effectuant la décomposition thermique des peroxy complexes, n'a été que moyennement satisfaisant. On a toutefois obtenu une séparation plus satisfaisante du tantale et du niobium, pour des rapports allant de 50 : 1 à 1 : 30, en extrayant la masse de fusion au bisulfate avec $(NH_4)_2Ox$ avant addition de H_2O_2, HCl et tanin. Pour un rapport tantale/niobium 1 : 1, la coprécipitation du niobium est réduite à 5%. En outre, on présente deux possibilités: 1) une récupération quantitative d'un précipité de tantale à faible concentration en oxalate et forte concentration en tannin, laissant 90% du niobium exempt de tantale en solution; 2) une récupération de 85% en tantale exempt de niobium, à forte concentration en oxalate et faible concentration en tanin. L'étude du processus de coprécipitation du niobium montre que les coefficients de distribution suivent un diagramme logarithmique; il se forme un vrai cristal mixte homogène.

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GRAVIMETRIC ANALYSIS OF TANTALOCOLUMBITES BY PRECIPITATION FROM HOMOGENEOUS SOLUTION*

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Summary—An analysis of complex tantalocolumbites has been carried out by precipitation from homogeneous solutions. A homogeneous precipitation of tungsten, titanium, tantalum and niobium by thermal decomposition of the soluble peroxytungstates, described in previous papers, is used. Corrections for incomplete precipitation and co-precipitation phenomena are applied on the basis of the experimentally found values. Silicon and tin are separated by volatilisation as fluoride and iodide, respectively. Iron is extracted by means of isopropyl ether and the rare earth metals are precipitated homogeneously from an oxalate solution. Manganese is precipitated as the ammonium phosphate. The results are in good agreement with an independent method, the standard deviations being within 1% for the major constituents.

INTRODUCTION

As shown in previous papers,[1–3] tungsten, titanium, tantalum and niobium can be separated and determined by precipitation from a homogeneous hydrogen peroxide solution. In the present work the method is tested on a number of synthetic and natural minerals, containing tantalum and niobium.

Qualitative analysis

Before carrying out the quantitative determination of three natural minerals, a spectrochemical qualitative analysis by means of a d.c. arc was effected. A quartz-prism spectrograph was used in the wavelength range of 2600–3950 Å and 2750–4200 Å. The results are given in Table I.

TABLE I.—Spectrochemical analysis of the minerals

Mineral	I	II	III
Major constituents	Nb, Ta, Fe, Mn	Nb, Ta, Fe, Mn, Ti	Nb, Ta, Fe, Mn, Ti, Cr, rare earths
Minor constituents	Ti, Si, Sn, W	W, Si, Sn, Mn	W, Sn, Si, Mg, Mo, Th
Traces	Cr, Zr, Al, Mo, Mg	Cr, Zr, Al, Mo, Pb	As, Zr, Al, Pb

Discussion of method

Because tin(IV) oxide and silica are only slightly attacked by a bisulphate fusion, and because the melt is only extracted with hydrogen peroxide-nitric acid, tin(IV) oxide and silica are found almost quantitatively in the residue. They are volatilised as the tetra-iodide and tetrafluoride, respectively; the content of silicon and tin is then computed by difference.

Tantalum, niobium and tungsten are separated by precipitation from a homogeneous hydrogen peroxide-nitric acid solution. They are separated and determined by homogeneous precipitation from a slightly alkaline hydrogen peroxide and from an oxalate-tannin-hydrogen peroxide medium. From the filtrate of the earth acids

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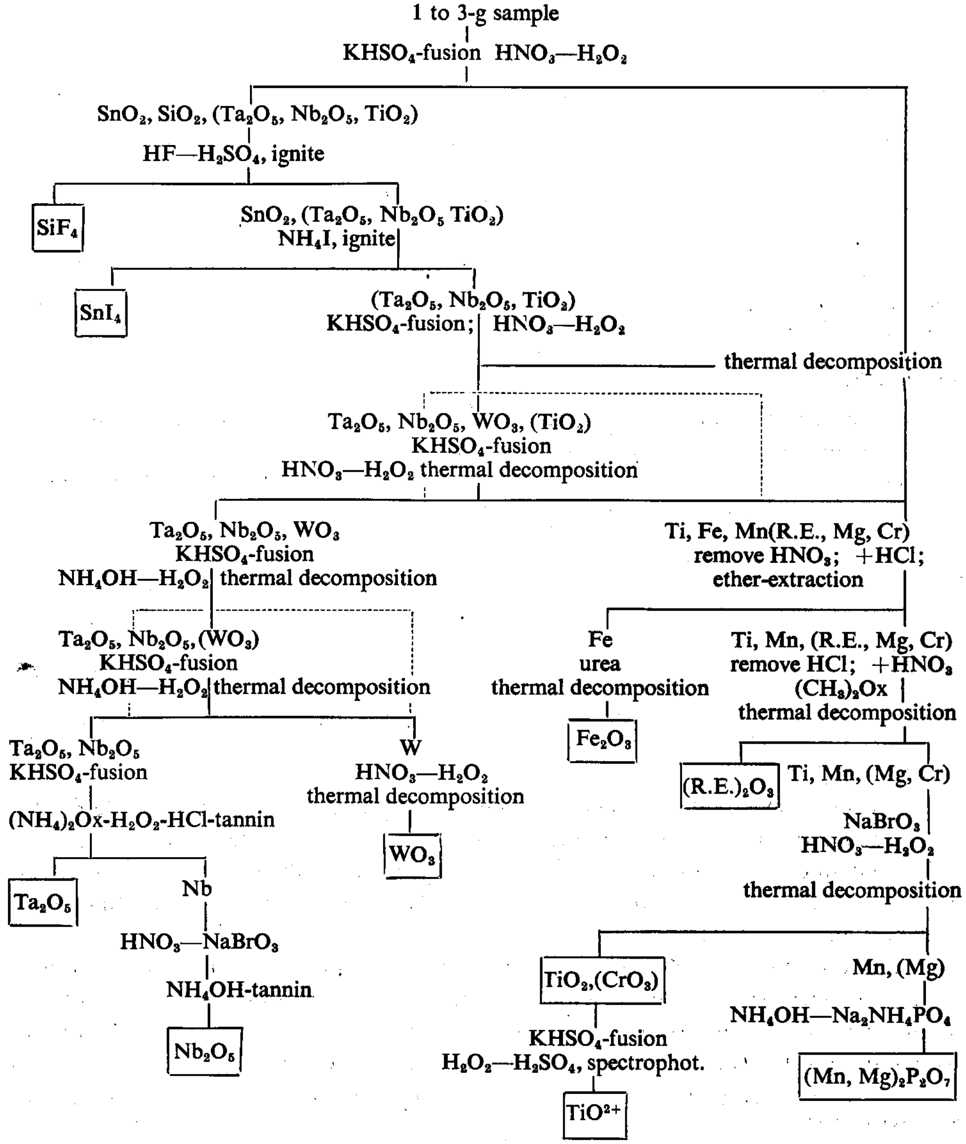
precipitation, iron is extracted with isopropyl ether, without manganese and titanium interference.[4] From a homogeneous hydrogen peroxide-nitric acid solution (pH 2·5) titanium precipitates practically quantitatively.[2] Manganese is obtained as manganese ammonium phosphate,[5] contaminated with small amounts of magnesium. The rare earths present in Mineral III are separated and determined as oxalates by a homogeneous precipitation with dimethyl oxalate.[6] In the presence of chromium (Mineral III), the precipitate of titanium is contaminated and was determined colorimetrically as peroxide in this precipitate.

An outline of the general scheme of the analysis is given in Fig. 1.

FIG. 1.—General scheme of analysis



Procedure. Fuse 1–3 g of finely powdered mineral with 5–15 g of bisulphate and dissolve the melt in hot 3% hydrogen peroxide. After neutralising with aqueous ammonia, acidify the solution to obtain 5*M* nitric acid. Filter the solution into an 800-ml beaker and transfer the precipitate to a platinum crucible. Add 4 ml of concentrated hydrofluoric acid and 1 ml of sulphuric acid and volatilise the silicon as silicon tetrafluoride. Take the residue twice to dryness with 2–3 ml of 14*M* nitric acid. Ignite the residue to constant weight at 950° to convert the sulphates and nitrates into the oxides. The silica content is found by difference. Add a ten-fold excess of ammonium iodide and 1 ml of hydriodic acid and stannictetriodide and heat at 475°. Repeat the process to ensure complete removal of tin. The loss in weight represents the amount of tin(IV) oxide. Fuse the residue with bisulphate and dissolve the melt in a few ml of 3% hydrogen peroxide and transfer the solution to the original filtrate. Heat at *ca.* 85° for 7 hr, in the presence of 0·1 g of selenous acid. Filter the hot solution and wash the precipitate with hot 1% nitric acid until free from sulphate. Incinerate and ignite the precipitate at 950° for 1 hr to constant weight. Fuse the mixed oxide residue with bisulphate in a silica crucible and leach the melt with 3% hydrogen peroxide and with dilute aqueous ammonia. Carefully adjust the pH of the solution to 7·5–8. After adding 0·1 g of selenous acid, heat the solution at 85° for 8 hr; tantalum and niobium are precipitated from this homogeneous solution. Collect the precipitate on a filter paper and wash with hot 2% alkaline ammonium nitrate until free from sulphate. Ignite the precipitate at 950° to constant weight as $(Ta, Nb)_2O_5$. For the determination of small amounts of titanium and tungsten repeat the precipitation steps from nitric acid and from slightly alkaline solution to reduce the coprecipitation of the latter. Evaporate the filtrate from the precipitation from alkaline medium, containing the bulk of the tungsten to *ca.* 150 ml and add 2 ml of 3% hydrogen peroxide and 75 ml of 14*M* nitric acid. Heat the solution at 60° for 2 hr. As soon as the precipitate has settled, filter from the hot solution, wash with hot 1% nitric acid, incinerate and ignite to constant weight at 900°. Weigh as WO_3. Fuse another two fractions, of *ca.* 125 mg, of the mixed oxides with bisulphate and transfer the crucible to an 800-ml beaker. Dissolve the melt in 120 ml of hot 5% ammonium oxalate solution. Add 120 ml of 12*M* hydrochloric acid, 2 ml of hydrogen peroxide (30%) and 2·5 g of tannin, dilute the solution to 600 ml. Heat for 7 hr at 85°. Filter the precipitate from the hot solution, wash with hot 2% ammonium chloride and ignite at 950° for 1 hr to constant weight. Weigh as Ta_2O_5. Evaporate the filtrate to *ca.* 200 ml. Remove the oxalate by adding a few ml of 14*M* nitric acid and a suitable amount of sodium bromate (3 g). Neutralise the solution with aqueous ammonia and add a ten-fold excess of tannin to the boiling solution. Boil for a few minutes until the precipitate settles. Filter and wash with hot 2% ammonium nitrate. Ignite the residue at 950° for 1 hr to constant weight as Nb_2O_5.

The filtrate from the earth acids precipitations contains titanium, iron, manganese and, in the case of Mineral III, chromium, rare earths and magnesium. Take almost to dryness and treat the residue with 50 ml of 12*M* hydrochloric acid. Repeat the operation to ensure complete removal of the nitric acid. Dissolve the residue in 300–800 ml of 8*M* hydrochloric acid and extract the iron repeatedly with isopropyl ether. Test for complete iron removal with thiocyanate. Shake the ether-phase three times with water to back-extract the iron. Neutralise the solution with aqueous ammonia and reacidify with dilute hydrochloric acid. Add 10 g of urea and boil the solution until neutrality is obtained; allow the precipitate to settle. To ensure complete precipitation of the iron, add a few ml of aqueous ammonia. Filter, wash and ignite the precipitate to constant weight as Fe_2O_3. For the determination of titanium, manganese and the rare earths, hydrochloric acid must be removed by the addition of 14*M* nitric acid and evaporation. Repeat the process twice. If rare earths are present, neutralise the solution with aqueous ammonia to pH 0·2, add 2 ml of 30% hydrogen peroxide and 30 ml of dimethyloxalate reagent solution (40 g of dehydrated oxalic acid dissolved in 100 ml methanol) to the solution and boil gently for 1 hr. Add an excess of 4 g of oxalic acid and boil for 0·5 hr. Filter the precipitate, wash with hot 2% oxalic acid and ignite at 950° to constant weight. Cover the crucible during cooling, and weigh quickly without removing the cover because the oxides absorb moisture and carbon dioxide from the air. Oxidise the excess of oxalate in the filtrate with sodium bromate in a nitric acid medium. Add 1 ml of hydrogen peroxide (30%), neutralise the solution to pH 2·5 and subject the peroxytitanates to thermal decomposition at 85° for 6 hr. Collect the precipitate and wash with hot 2% ammonium nitrate. Ignite the precipitate to TiO_2 at 950°. In presence of much chromium fuse the precipitate and extract with sulphuric acid. Add a few ml of hydrogen peroxide (30%) and determine the titanium by spectrophotometry at 410 mμ. To the filtrate from the titanium precipitation add aqueous ammonia and disodium ammonium phosphate. Collect the precipitate on a Gooch crucible and redissolve with sulphuric acid. Reprecipitate manganese and magnesium, if present, as ammonium phosphates. Collect the precipitate and ignite to constant weight at 650° as $(Mn, Mg)_2P_2O_7$. The tantalum, niobium, tungsten and titanium precipitates are filtered on SS 589^3 and the iron precipitate on SS 589^1 filter papers.

The results for tantalum, niobium, tungsten, titanium and manganese were corrected for incomplete recovery and for coprecipitation, corrections being applied according to the experimentally found values.[1-3]

TABLE II.—Analysis of synthetic mixture

Sample, *g*	SiO_2, %	SnO_2, %	Ta_2O_5, Nb_2O_5, WO_3, %	Ta_2O_5, Nb_2O_5, %	TiO_2, %		WO_3, %	Ta_2O_5, %	Nb_2O_5, %
					Colorimetry	Gravimetry			
1·0005	6·38	—	65·26	64·43	1·73^{6}	—	—	29·88 28·83 28·91	35·06 34·83 34·54
1·0014	6·07	—	65·47	64·05	1·67^{1}	—	—	—	—
1·0009	6·33^{5}	6·22^{5}	65·04	64·15	—	1·65^{8}	—	—	—
3·0014	6·40	6·30^{5}	64·95	64·02	—	1·70^{5}	0·96^{5}	—	—
Mean, %	6·30 ± 0·07^{5}	6·26^{5} ± 0·03^{9}	65·13 ± 0·12	64·16 ± 0·10	1·70^{5} ± 0·03^{8}	1·70^{0} ± 0·01^{4}	0·96^{5}	29·21 ± 0·33^{5}	34·81 ± 0·15
Taken, %	6·24	6·25	65·05	64·21	1·66^{8}		0·83^{5}	29·15	35·02

Fe_2O_3 = 10·01%; Mn_2O_3 = 10·84%.

TABLE III.—Analysis of Mineral I

Sample, g	SiO_2, %	SnO_2, %	FeO, %	MnO, %	TiO_2, %	WO_3, %	Ta_2O_5, %	Nb_2O_5, %	Sum, %
1·0002	0·74	0·62	7·71	12·90^2	0·91^0	—	35·49^8 35·44^9	43·04^5 43·22^5	—
1·0008	0·88	0·58	7·69^2	12·99^0	0·87^5	—	35·68^3 35·53^7	43·25^1 43·15^2	—
1·0000	0·88	0·49	7·68^1	12·83^4	0·74^1	—	35·29^8 35·57^1	(44·83^6) 42 91^7	—
1·0004	0·76	0·54	—	—	—	—	—	—	—
3·0005	0·89	0·42	7·66^1	12·95^3	0·82^2	—	35·20^8 35·31^7	42·84^0 42·94^0	— —
3·0009	0·66	0·43	7·70^3	12·88^0	0·87^1	—	35·25^0 35·48^2	42·86^3 42·69^7	—
Mean, %	0·80 ± 0·03^9 s = ±0·09^5	0·51^5 ± 0·03^3 s = ±0·08^1	7·69 ± 0·00^9 s = ±0·02^0	12·91 ± 0·02^6 s = ±0·05^8	0·84^5 ± 0·01^8 s = ±0·04^1	—	35·43 ± 0·04^9 s = ±0·15^5	42·99 ± 0·10^7 s = ±0·32^0	101·1^8
Analysis[a]	0·86	0·48^2	7·72	13·32	0·90	0·22	35·32	42·77	101·5^9

[a] Analysis by Société Genérale Métallurgique de Hoboken.

TABLE IV.—Analysis of Mineral II

Sample, g	SiO_2, %	SnO_2, %	FeO, %	MnO,[a] %	TiO_2, %	WO_3, %	Ta_2O_5, %	Nb_2O_5, %	Sum, %
1·0019	0·73^5	0·61	11·27^0	10·24^5	2·45	—	25·49^2 25·51^2	47·17^0 47·10^0	—
1·0284	0·82	0·50	(10·63)	(9·26)	(2·11)	—	25·88^5 25·73^9	47·02^5 47·66^6	—
1·0004	0·97	0·41	11·35^2	10·20^5	2·29	—	25·54^0	47·80^1	—
							25·67^0	47·96^1	
2·9997	0·82	0·46^5	11·28^0	10·29^4	2·18^8	0·84^2	25·65^8 25·75^4	47·88^8 47·99^8	—
2·9999	0·68	0·48^5	11·24^3	10·28^2	2·30^1	0·97^8	25·83^7 25·85^9	47·84^5 47·71^1	—
Mean, %	0·80^5 ± 0·04^5 s = ±0·10^1	0·49^5 ± 0·03^8 s = ±0·07^8	11·28^5 ± 0·02^4 s = ±0·04^7	10·25^5 ± 0·02^0 s = ±0·04^0	2·26^0 ± 0·04^1 s = ±0·08^1	0·91 ± 0·06^8	25·69^5 ± 0·04^6 s = ±0·14^5	47·61^5 ± 0·11^0 s = ±0·35^0	99·32^0
Analysis[b]	0·28	0·54^6	11·55	10·24^5	2·29	1·02	25·69	47·30	98·92^1

[a] Magnesium present (<0·2%) determined as manganese.

[b] Analysis by Société Genérale Métallurgique de Hoboken.

TABLE V.—Analysis of Mineral III

Sample, g	SiO_2, %	SnO_2, %	FeO, %	MnO,[a] %	TiO_2,[b] %	WO_3, %	Ta_2O_5, %	Nb_2O_5, %	Rare earths R_2O_3, %	CrO_3,[b] % (minimum)	Sum, %
1·0006	1·13	1·15	12·03^1	10·22^5	5·43^9	—	23·10^5 23·03^6	36·04^4 36·26^2	4·51	1·55	
1·0001	0·95	0·92	12·13^8	10·17	5·57^7	—	23·63^6 23·01^6	37·00^3 36·60^4	4·55	1·52	
0·9997	0·96	1·00	12·10^3	10·33	5·50^4	—	23·61^7 23·18^0	36·98^8 36·95^8	4·45	1·44^5	
3·0004	0·93	0·95^5	12·00^0	10·18	5·44^3	0·72^6	23·41^3 23·29^8	36·81^9 36·74^5	4·48	1·42	
2·9999	0·95^5	1·13^5	12·00^7	10·20^5	(4·89^4)	0·83^3	23·70^0 23·78^1	36·87^0 (39·76^3)	4·53	(2·06)	
Mean, %	0·98^5 ± 0·02^3 s = ±0·05^0	1·03 ± 0·04^7 s = ±0·10^5	12·05^5 ± 0·02^7 s = ±0·06^1	10·22 ± 0·02^9 s = ±0·06^5	5·46 ± 0·01^1 s = ±0·02^2	0·78 ± 0·05^4	23·38 ± 0·09^4 s = ±0·29^8	36·70 ± 0·11^6 s = ±0·34^8	4·50^5 ± 0·01^8 s = ±0·04^0	1·49 s = ±0·06^2	96·60^5
Analysis[c]	0·73	1·29^5	12·22	9·20	5·27	1·06	23·91	35·73	—	—	89·41^5

[a] Magnesium present determined as manganese.

[b] Titanium content determined colorimetrically, the difference between the colorimetric and gravimetric determination being given as chromium.

[c] Analysis by Société Genérale Métallurgique de Hoboken.

The double precipitation used for the analysis of the 3-g samples reduces the coprecipitation of titanium and tungsten to a considerable extent. When calculating the weighed mean values and the standard deviations for the titanium and tungsten, a three-fold weight was given to these results.

Before carrying out the analyses of the 3 minerals, the tantalum, niobium, tungsten, titanium, silicon and tin contents of a synthetic mixture were determined following the same procedure. The results are given in Tables II, III, IV and V.

From Tables III–V it appears that the results are mostly in good agreement with the results of an analysis performed elsewhere by an independent procedure. The deviation of the results of the major elements (tantalum, niobium, iron and manganese) are within 1%. The larger deviation in the case of tungsten and titanium is obviously caused by the fact that the contents are only small in the presence of large amounts of earth acids. Chromium interferes with the gravimetric determination of titanium.

Acknowledgments—Thanks are due to the "Société Générale Métallurgique de Hoboken" for providing the samples of tantalocolombites. The technical assistance of Miss M. Helsen is gratefully acknowledged.

Zusammenfassung—Eine Analyse komplizierter Tantalocolumbite wurde mittels Fällungen aus homogener Lösung ausgeführt. Homogene Fällung von Wolfram, Titan, Tantal und Niob durch thermische Zersetzung der löslichen Peroxywolframate wird verwendet, wie in den vorhergehenden Arbeiten beschrieben. Korrekturen für unvollständige Fällung und Mitfällung werden auf Grund der experimentell gefundenen Werte angebracht. Silicium und Zinn werden durch Abdestillieren als Fluorid bzw. Jodid abgetrennt. Eisen wird mit Isopropyläther extrahiert, die seltenen Erden homogen aus Oxalatlösung gefällt und Mangan als Ammoniumphosphat niedergeschlagen. Die Ergebnisse stimmen gut mit einer unabhängigen Methode überein, die Standardabweichungen für die Hauptbestandteile liegen unter 1%.

Résumé—On a effectué une analyse de tantalocolumbites complexes par précipitation à partir de solutions homogènes. On emploie une précipitation homogène des tungstène, titane, tantale et niobium par décomposition thermique des peroxytungstates solubles, qui a été décrite dans des mémoires antérieurs. Sur la base des valeurs trouvées expérimentalement, on applique des corrections pour la précipitation incomplète et pour les phénomènes de coprécipitation. Le silicium et l'étain sont séparés par volatilisation à l'état de fluorure et d'iodure. Le fer est extrait au moyen d'éther isopropylique et les métaux des terres rares sont précipités en milieu homogène à partir d'une solution oxalique. On précipite le manganèse avec le phosphate d'ammonium. Les résultats sont en bon accord avec une méthode indépendante, les écarts types étant à 1% près pour les principaux constituants.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XVII*

DETERMINATION OF ZINC AND CADMIUM IN THE PRESENCE OF EACH OTHER

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Summary—A new method for separating cadmium from zinc by precipitation as $Cd(phen)_2I_2$ is reported. Even very small amounts of zinc can be determined complexometrically in highly ammoniacal media by back-titration of an added excess of DCTA with calcium(II) using Methylthymol Blue as indicator.

CADMIUM and zinc form complexes with EDTA of almost identical stability (log $K_{CdY} = 16{\cdot}46$, log $K_{ZnY} = 16{\cdot}50$), so it is necessary to separate them for their complexometric determination in mixtures. Some years ago Přibil[1] proposed diethyldithiocarbamate for precipitation of cadmium after the complexometric determination of the sum of zinc and cadmium in slightly ammoniacal solutions. Kinnunen and Wennestrand[2] removed small amounts of cadmium by precipitation with thiourea. The adsorbed zinc was then removed by extracting its thiocyanate complex into an ether-amyl alcohol mixture. Recently, Fabregas, Prieto and Garcia[3] masked cadmium with a lead-EDTA complex. The displaced equivalent amount of lead was then precipitated as sulphate and removed from the solution by filtration. In the filtrate zinc was determined by EDTA titration with Eriochrome Black T as indicator. The results are satisfactory up to the weight ratio Zn:Cd = 1:17. Only one method for the determination of cadmium in the presence of zinc without previous separation is known; Flaschka and Ganchoff[4] titrated cadmium with ethyleneglycol-bis-(β-aminoethylether)-*N*,*N*-tetra-acetic acid (EGTA) solution, using copper sulphate as indicator. The end-point was detected spectrophotometrically by the appearance of the first traces of a blue copper-EGTA complex. With this method cadmium can be determined up to a 1:500 ratio of Cd:Zn.

None of the mentioned methods is, however, suitable for the determination of zinc in the presence of high concentrations of cadmium. Because one can hardly expect to find a specific masking agent for cadmium, we have searched for a new method for its separation from zinc. From preliminary experiments it was ascertained that cadmium precipitates quantitatively in a well filtrable form as $Cd(phen)_2I_2$. We have now found simple conditions where no adsorption of zinc occurs. The precipitation of cadmium as a phenanthroline-iodide complex is much more selective than the analogous precipitation as a phenanthroline-thiocyanate complex which has been used for the gravimetric determination not only of cadmium but also of copper, manganese, nickel and cobalt.[5]

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* Part XVI: *Talanta*, 1964, **11**, 1545.

The last three elements do not precipitate at all in the presence of iodide with phenanthroline. Amounts of cadmium even smaller then 5 mg can be separated by the proposed method.

EXPERIMENTAL

Reagents:

0·1*M o-Phenanthroline solution:* Add 1·8 g of solid *o*-phenanthroline to 50 ml of water, dissolve by dropwise addition of 1*M* hydrochloric acid, then dilute to 100 ml.

0·05*M DCTA solution:* Dissolve 17·72 g of 1,2-diaminocyclohexanetetra-acetic acid (J. R. Geigy, Basel, Switzerland) in hot water by adding 130 ml of 1*M* sodium hydroxide. Dilute to 1 litre. The pH of the solution should be *ca.* 5. Standardise by a complexometric titration with lead nitrate using Xylenol Orange as the indicator.

Other reagents: 0·05*M* cadmium nitrate, 0·05*M* zinc nitrate (prepared by dissolving metallic zinc in nitric acid), 0·05*M* calcium chloride (prepared by dissolving calcium carbonate in hydrochloric acid), solid potassium iodide, solid urotropine, Methylthymol Blue (1:100 with solid potassium nitrate).

Precipitation of cadmium as $Cd(phen)_2I_2$

To precipitate cadmium in a well defined crystalline form without adsorption of zinc great care has to be taken. The original pH of the solution must be 2·5–3·5, otherwise a voluminous precipitate adsorbing zinc is formed; also, the washing out of the precipitate on the filter is very important. The following procedure is considered to be most advantageous. Adjust the pH of the solution containing cadmium and zinc to 2·5–3·5, add 0·5–1·0 g of potassium iodide and heat to boiling. Add, dropwise, 0·1*M o*-phenanthroline solution until no further precipitate is formed. Cease boiling the solution and adjust the pH to 4·5–5 with solid urotropine. Intense stirring with a glass rod speeds up the formation of a crystalline precipitate, which settles easily. With small amounts of cadmium (< 5 mg) let the solution stand for 1 hr in a water-bath. Filter the precipitate through a paper filter (Black or White ribbon) and wash out the precipitate on the filter 8–10 times with a warm (50–60°) wash solution.* All of the zinc is in the filtrate.

Determination of zinc

In slightly acidic media zinc is completely complexed by *o*-phenanthroline,[6] but in strongly ammoniacal media the $Zn(phen)_2^{2+}$ complex is broken down. An ammonia-ammonium chloride buffer of pH 9–10, suitable for titrations with Eriochrome Black T, is not sufficiently concentrated and aqueous ammonia is required. Under these conditions the titration with EDTA does not have a sufficiently sharp change of pZn^{2+} at the equivalence point and it is better to use an indirect determination with DCTA solution.

Procedure. To the filtrate from the separation of cadmium add an excess of 0·05*M* DCTA (at least 30%) and 20–30 ml of concentrated aqueous ammonia. Add Methylthymol Blue and back-titrate with a solution of 0·05*M* calcium chloride to an intense blue coloration. The end-point is very sharp and reversible. A greater excess of aqueous ammonia than that given has no influence on the titration.

A number of determinations of zinc in the presence of small and high concentrations of cadmium have been made following the procedure. The results are shown in Table I.

TABLE I.—DETERMINATION OF ZINC AND CADMIUM

Taken, *mg*		Found, *mg*		Difference, *mg*		Ratio of Cd:Zn, *mg*
Cd	Zn	Cd	Zn	Cd	Zn	
56·50	10·24	56·50	10·25	0	+0·01	5·5:1
5·65	34·00	5·90	33·90	+0·25	−0·10	1:55
2·82	68·00	3·37	67·80	+0·55	−0·20	1:20
1·12	68·00	1·57	67·92	+0·45	−0·08	1:43
84·70	1·70	85·00	1·54	+0·30	−0·16	55:1
141·20	1·70	141·90	1·64	+0·70	−0·06	85:1
5·65	74·99	6·51	74·70	+0·86	−0·29	1:12
28·25	17·00	28·70	16·83	+0·45	−0·17	1·5:1
5·65	3·40	6·40	3·08	+0·75	−0·32	2:1
5·65	340·00[a]	—	338·00	—	2·00	1:60

[a] 1/10th Aliquot for determination of Zn.

* 10 ml 0·1*M o*-phenanthroline in 500 ml of water.

DISCUSSION

The separation of cadmium as $Cd(phen)_2I_2$ is rather selective. Manganese, nickel and cobalt are not precipitated, but copper and lead must be absent. This offers a further possibility of determining cadmium gravimetrically as $Cd(phen)_2I_2$. In this case, iron(III), lead, *etc.*, could be screened with EDTA. This enables some simplified analyses of alloys containing cadmium, zinc and other elements to be made. These practical applications will be discussed elsewhere.

Zusammenfassung—Eine neue Methode zur Trennung von Cadmium und Zink durch Fällung von Cadmium als Cd-Phenanthrolin-Jodid $Cd(phen)_2J_2$ wird angegeben. Auch sehr kleine Zinkmengen werden in stark ammoniakalischem Medium komplexometrisch durch Rücktitration von DCTA mit Calciumsalz bestimmt. Methylthymolblau wird als Indikator verwendet.

Résumé—On décrit une nouvelle méthode pour séparer le cadmium du zinc, par précipitation à l'état d'iodure de cadmium-phénanthroline, $Cd(Phen)_2I_2$. Même de très petites quantités de zinc sont dosées par complexométrie en milieu fortement ammoniacal, par titrage en retour du DCTA au moyen d'un sel de calcium. On prend pour indicateur le bleu de méthylthymol.

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THE DETERMINATION OF ACETONE IN BUTANONE-2 BY PHASE SEPARATION

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Summary—Binary solutions of acetone in butanone-2 have been analysed by adding a constant amount of water and determining the temperature at which phase separation takes place. Because butanone-2 and water have a lower critical solution temperature, solutions are clear at lower temperatures and opalescent at higher temperatures. The weight percent of acetone in the original binary solution of ketones is a function of the phase-separation temperature, enabling the analyst to construct a calibration curve and determine unknown solutions directly. The error is about 0·1 absolute %.

MANY binary solutions exhibit a miscibility gap and, at certain concentrations, separate into two phases. Each phase is, itself, a binary solution. As the temperature of the system is increased, the composition of each phase usually approaches that of the other. Normally, at some temperature, the compositions of the phases become the same and the components become miscible in all proportions. This temperature is called the upper critical solution temperature. Less commonly, the liquid components become more soluble in each other as the temperature decreases and are completely miscible in all proportions below a temperature minimum. Such a temperature minimum is called a lower critical solution temperature. Some systems have both lower and upper critical solution temperatures.

Small amounts of impurities have a profound effect on the solubility curves of partially miscible binary solutions.[1] As long ago as 1914, Findlay suggested the critical solution temperatures as a criterion of purity,[2] and phase separation is the basis of a number of analytical methods, including the cloud-point method of determining water[3–7] and binary mixtures,[8–9] and the cloud- and aniline-point methods of characterising petroleum products[10] and fats.[11]

Because many binary solutions have miscibility gaps which are displaced by any one of an indefinite number of impurities, the phenomenon of phase separation should be capable of much wider analytical application than it now enjoys. This work is an example of the application of the phenomenon of phase separation to the subtle analytical problem of the accurate determination of the ratio of acetone to butanone-2 in binary solutions. It is novel in the application of the lower critical solution temperature to an analytical problem.

THEORY

Butanone-2 and water have an upper and a lower critical solution temperature. Because the lower critical solution temperature is more readily accessible, we will consider it in the following discussion. Acetone, being completely miscible with both

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butanone-2 and water, increases their mutual solubility and increases the lower critical solution temperature. If a calibration curve were constructed of the critical solution temperature of butanone-2 in ternary solutions with water and acetone, as a function of the ratio of acetone to butanone-2, unknowns could be determined by comparison. Critical solution temperatures would be determined by varying the amount of water in combination with a given ratio of acetone to butanone-2 and recording the minimum temperature of phase separation. The method would not be useful for determining the amount of water in any ternary solution because the temperature of phase separation is not very sensitive to small changes in composition of the system with respect to water.

Because the shape of the solubility curve is flat over a wide composition range in the region of the critical solution temperature, a considerable experimental simplification can be achieved. A convenient composition near the critical solution composition is selected, keeping the amount of water constant throughout, and the temperature of phase separation is determined. This avoids the necessity of determining the entire lower part of the solubility curve. The exact critical solution composition is not selected because it is not accurately known and it may change with increasing amounts of acetone.

EXPERIMENTAL

Reagents

Reagent-grade acetone and butanone-2 and distilled water were used throughout.

Procedure

Ten ml of a binary solution of acetone in butanone-2 are put in a test-tube with an equal amount of water. After cooling the solution below the temperature at which it becomes homogeneous and clear, it is allowed to warm slowly and, at the appearance of the first slight haze, the temperature is recorded to the nearest 0·1°. To prevent separation into two layers, the solution is stirred using a magnetic stirrer and a short stirring bar rotating at low speed. If turbidity occurs above room temperature, a water bath is used. In all cases, the rate of heating is less than 1° per min.

RESULTS

Fig. 1 is the calibration curve of the solution temperature of ternary solutions of acetone, butanone-2 and water at constant water composition. The temperature is plotted as a function of the weight percent of acetone in the original binary solution to which the water was added. The lower limitation of the curve is the point at which ice begins to separate from the water-rich phase and the upper limit is the boiling point of the organic rich phase. These are about −6 and 60°, respectively. The calibration curve has not been taken to these extremes because at the lower temperature, bubbles, arising from stirring, interfere with the observation of turbidity. They do not float out because of the increased viscosity of the solution at low temperatures. The upper extreme was avoided to prevent slight changes in composition from vaporisation. Any solution outside the useful composition range can be adjusted by standard addition of one of its components.

Observation of phase separation

Because the refractive indices of the phases are not very different, the turbidity which appears as the system goes from one to two phases is light. Viewed against a black background with cross illumination, phase separation produces a slight haze which, despite its unspectacular nature, is unmistakable and occurs within 0·1°. Stirring should be slow and intermittent up to the point of phase separation to prevent interference by bubbles.

The solution temperatures were approached from both lower and higher temperatures. Agreement was within 0·4°, indicating little kinetic lag. For maximum reproducibility, only those solution temperatures observed on increasing the temperature were used for analytical purposes.

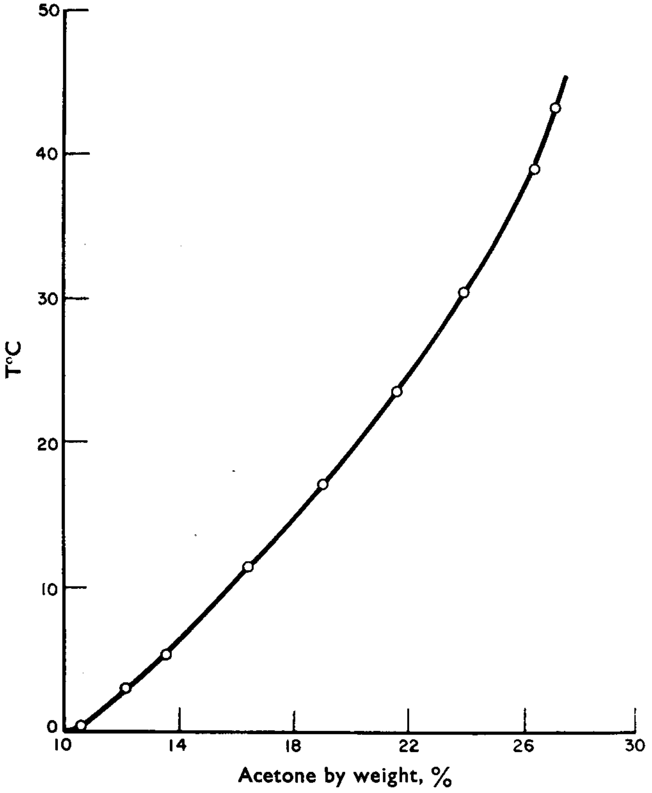

FIG. 1.—The temperature above which phase separation takes place for solutions of acetone, butanone-2 and water. The composition is constant with respect to water.

Potential accuracy of the method

The phase separation temperature can be determined with an error of less than 0·2° for replicate samples. The minimum slope of the calibration curve is 0·65% per degree and its maximum slope is 0·21% per degree at higher temperatures. Therefore, the minimum error should be about 0·13% at lower temperatures and 0·04% at higher temperatures. The extreme sensitivity of the solubility of butanone-2 in water to the presence of acetone makes this method one of high potential accuracy.

Comparable methods of analysing binary solutions are by density and refractive index measurements. The difference in density between acetone and butanone-2 is 0·0140 g/ml.[12] Assuming a minimum error of 0·0002 g/ml in density measurements, the error is about 1·4%.

The difference in refractive index between acetone and butanone-2 is 0·0216.[12] Assuming a minimum error of 0·0002 in refractive index measurement, the resulting analytical error is slightly less than 1%.

Interferences

All foreign substances interfere with analysis by phase separation. Like the comparable physical methods of density and refractive index, analysis by phase separation is strictly applicable only to binary solutions or solutions in which the amount of interfering substance is absolutely constant from one sample to the next.

One common impurity, water, does not interfere to a serious extent if its concentration is low. Because of the flat shape of the solubility minimum, small variations in the ratio of water to the organic components do not cause large changes in the solution temperature. The addition of 0·1 ml of water in excess of the usual amount increases the solution temperature by 0·1° for a solution showing phase separation at 30·4°. The addition of 0·1 ml of ethanol to the same system raised the solution temperature by more than 6°.

If the amount of water, the most common impurity, is less than 1% there will be no noticeable effect on the solution temperature. The amount of water which may be tolerated varies with the composition of the solution being analysed because the shape of the solubility curve varies with composition.

Applications

Like density and refractive index, phase separation will usually be useful only when the solutions being analysed are known to be binary solutions. An example is in the determination of the theoretical plates of a distilling column by analysis of the distillate and residue of a solution which is known to be binary.

Routine analysis is most convenient by phase separation when acceptable limits of concentration have been set. One constant temperature bath can be set to the temperature of the lower limit of concentration and another to the temperature of phase separation of the upper limit. Duplicate samples can be allowed to come to temperature equilibrium, one in each bath. If one is turbid and the other is not, the sample is within the concentration limits specified.

Phase separation is a method of cross checking other methods applicable to binary solutions. If a solution is assumed to be binary but is contaminated by a third substance, density, refractive index or phase separation measurements, taken singly, will give false results. If analysis by all three methods gives results which check with each other, the original solution was binary.

CONCLUSION

Analysis of binary solutions by phase separation at a lower consolute temperature has been illustrated by the system acetone in butanone-2. The method has the advantages of accuracy, simplicity and generality. It has the disadvantage of great susceptibility to interference.

Zusammenfassung—Binäre Lösungen von Aceton in Butanon-2 wurden analysiert durch Zusatz einer konstanten Wassermenge und Bestimmung der Temperatur, bei der Phasentrennung eintritt. Da Butanon-2 und Wasser eine untere kritische Lösungstemperatur haben, sind die Lösungen bei tiefen Temperaturen klar und bei höheren trübe. Der

Gewichtsprozentsatz von Aceton in der binären Ketonlösung ist eine Funktion der Trübungstemperatur. Damit kann man eine Eichkurve aufstellen und unbekannte Lösungen direkt bestimmen. Der Fehler beträgt etwa 0,1 % absolut.

Résumé—On a analysé des solutions binaires d'acétone et de butanone-2, par addition d'une quantité constante d'eau et détermination de la température à laquelle on observe une séparation de phases. La butanone-2 et l'eau ayant une température critique inférieure de miscibilité, les solutions sont claires aux plus basses températures, et opalescentes aux températures plus élevées. Le pourcentage en poids de l'acétone dans la solution binaire initiale des cétones est une fonction de la température de séparation des phases. L'analyste peut ainsi construire une courbe d'étalonnage et doser directement des solutions inconnues. L'erreur est d'environ 0,1 % absolu.

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ANION-EXCHANGE SEPARATION OF BERYLLIUM, VANADIUM AND OTHER ELEMENTS FROM LARGE AMOUNTS OF URANIUM

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Summary—A method is described for the anion-exchange separation of small quantities of beryllium, vanadium, magnesium, calcium, aluminium, gallium and indium from gram-amounts of uranium. For this purpose, a medium consisting of 95% methanol and 5% 5*M* nitric acid is passed through a resin bed of Dowex 1, X8. By subsequent washing of the resin with a methanol-nitric acid mixture of the same composition, these metal ions are preferentially eluted from the column, whereas uranium is still retained by the anion exchanger. In the eluates the elements are determined by means of spectrophotometric or titrimetric procedures.

INTRODUCTION

RESEARCH work carried out by Buchanan and Faris[1] has shown that uranium is only weakly adsorbed on strongly basic resins from aqueous nitric acid solutions. This fact has been employed to separate uranium, together with other weakly adsorbed elements, from those which are strongly adsorbed, such as thorium and bismuth.

When the nitrate concentration of such solutions is increased, as, for instance, by adding the nitrates of ammonium,[2] aluminium[3,4] or nickel,[4] the uptake of uranium by these resins is considerably enhanced, and quantitative adsorption can be achieved. These methods, however, suffer from the disadvantage that large amounts of salts will be present in the effluent in which the non-adsorbable elements have to be determined. In addition, gross quantities of vanadate and other anions would compete with uranium for resin sites, thus limiting the quantitative retention of uranium.

In mixed aqueous-organic solvent systems, in which the distribution coefficients of most elements are considerably higher than in pure aqueous nitric acid solutions, uranium is also more strongly adsorbed, as has been shown in detail by Korkisch and coworkers.[5,6]

Based on these observations an attempt has been made to find a means of separating large amounts of uranium as the nitrate from milligram or microgram quantities of other metal ions, such as beryllium and vanadium, which might be present in uranium used as a reactor fuel, or in uranium compounds obtained after the processing of uraniferous materials such as carnotite ores.

EXPERIMENTAL

Reagents

Ion-exchange resin: The strongly basic anion exchanger Dowex 1, X8 (100–200 mesh; nitrite form) was used.

Standard solutions of uranium and other elements: 5*M* nitric acid solutions of the nitrates, of exactly known element content, were employed.

Organic solvent: Reagent-grade methanol.

Wash solution: 95% (v/v) methanol- 5% (v/v) 5*M* nitric acid.

Apparatus

Ion-exchange columns: The column operations were carried out in resin columns of 75 cm length and a diameter of 1 cm.

Spectrophotometer: For the spectrophotometric determination of all elements investigated, with the exception of uranium which was determined fluorimetrically, the Beckman Model B spectrophotometer was employed.

Fluorimeter: The photoelectric fluorimeter employed was a Galvanek Morrison Fluorimeter, Mark V.

Quantitative determinations

Determination of uranium: The quantitative determination of uranium in the effluents was performed fluorimetrically by means of a procedure described by Schönfeld, El Garhi, Friedmann and Veselsky.[7]

Determination of other elements: The convenient and accurate photometric procedures described by Sandell[8] and by Snell and Snell[9] were used to determine microgram amounts of all metal ions investigated except beryllium, for the assay of which the following method was developed:

To 1 ml of 5*M* nitric acid, containing not more than 20 μg of beryllium, are added 1 ml of a 1% solution of Neothoron in methanol and 1 ml of 0.1*M* EDTA solution (disodium salt), and the solution is diluted to 10 ml with 2*M* sodium acetate solution. Spectrophotometric measurement is carried out at 570 mμ.

Under these experimental conditions, Beer's law is obeyed from 0 to 20 μg of beryllium/10 ml of measured solution. The addition of EDTA reduces the number of interfering elements considerably, so that in practice only appreciable amounts of aluminium and iron interfere slightly. Uranyl ions would cause strong interference when present, but they are removed by the ion-exchange step.

The determination of milligram quantities of the elements investigated was performed by using suitable titrimetric methods, mostly employing titration with 0.01 or 0.001*M* solutions of EDTA.

Column operations

Through the resin bed, pretreated with 100 ml of the wash-solution, were passed 20 ml of a mixture consisting of 1 ml of 5*M* nitric acid (containing uranium and the other element to be separated from uranium) and 19 ml of methanol, at a flow rate of 0.5 ml/min. The column was washed at the same rate with the wash solution, effecting the preferential elution of the second element; uranium passes only slowly down the column. When performing the test runs, each 5-ml portion of the effluent was collected and analysed for the metal ion in question and for uranium. After complete elution of the element, uranium is removed from the column by washing with a mixture consisting of 50% methanol–45% water–5% 5*M* nitric acid. The composition of this mixture is not critical, but after elution the resin can be regenerated better than if aqueous nitric acid only were used. In addition, excessive bubble formation is prevented.

RESULTS AND DISCUSSION

In Table I, the results of a series of separation experiments, carried out according to the ion-exchange procedure described above, are recorded. In all cases quantitative separation can be achieved, even when 10 g of uranium are present in the sorption solution. To demonstrate the effectiveness of this separation procedure the break-through volumes of uranium and the elution volumes of the other elements have been included in the table. As the elution volume, the ml of wash solution necessary to elute completely the element in question was taken. The break-through volumes of uranium are the ml of effluent in which uranium is detectable by means of the fluorimetric procedure.[7] Because the elution and break-through volumes are always more or less distinct, quantitative separation can thus be ensured.

Attempts to separate cadmium or strontium from uranium were unsuccessful.

Investigations carried out using other aliphatic alcohols in place of methanol have shown that in these solvents the separation of uranium from the metal ions investigated here is less advantageous, because of stronger adsorption by the resin.

TABLE I.—SEPARATION OF BERYLLIUM, VANADIUM(V), MAGNESIUM, CALCIUM, ALUMINIUM, GALLIUM AND INDIUM FROM URANIUM

Amount of uranium taken, *g*	Amount of other element taken, *mg*	Amount of other element recovered, *mg*	Elution volume, *ml*	Break-through volume of uranium, *ml*
10	Be 5	5.007	80	100
5	Be 5	5.001	80	130
1	Be 5	5.002	80	130
1	Be 0.1	0.098	80	130
1	Be 0.01	0.010	80	130
0.1	Be 0.01	0.010	80	180
10	V 5	4.98	80	90
5	V 0.1	0.10	60	130
0.05	V 12.	12.02	120	225
0.1	V 5.	5.004	80	250
1	Mg 5	5.01	80	150
0.5	Mg 5	4.98	80	150
1	Ca 5	5.01	90	140
0.5	Ca 5	5.02	90	140
1	Al 10	9.987	80	130
1	Al 0.1	0.101	80	130
1	Al 5	5.01	80	130
1	Ga 4	4.01	90	130
7	Ga 0.1	0.10	90	120
1	Ga 5	5.008	90	130
1	In 5	5.01	100	130
1	In 0.1	0.10	100	130
0.5	In 5	4.99	100	130

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Zusammenfassung—Es wird eine Methode beschrieben mittels der geringe Mengen an Beryllium, Vanadium, Magnesium, Calcium, Aluminium, Gallium und Indium von Grammengen Uran durch Anionenaustausch getrennt werden können. Zu diesem Zweck wird eine Lösung bestehend aus 95% Methanol und 5% 5*M* Salpetersäure durch ein Harzbett aus Dowex 1, X8 fließen gelassen. Beim darauffolgenden Waschen des Harzes mit einer Methanol-Salpetersäuremischung derselben Zusammensetzung werden diese Metallionen bevorzugt von der Säule eluiert während Uran weiterhin vom Anionenaustauscher festgehalten wird. In den Eluaten werden dann die Elemente mittels spektrophotometrischer oder titrimetrischer Verfahren quantitativ bestimmt.

Résumé—On décrit une méthode de séparation, par échange anionique, de petites quantités de beryllium, vanadium, magnésium, calcium, aluminium, gallium et indium, à partir de quantités d'uranium de l'ordre du gramme. Dans ce but on fait passer, à travers une couche de résine Dowex 1, X8, un milieu constitué de 95% de méthanol et 5% d'acide nitrique 5*M*. Par lavage ultérieur de la résine avec un mélange méthanol-acide nitrique de même composition, on élue préférentiellement ces ions métalliques de la colonne, cependant que l'uranium reste retenu par l'échangeur anionique. Dans les éluats, les éléments sont dosés par des techniques spectrophotométriques ou volumétriques.

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A SELECTIVE EXTRACTION SYSTEM FOR TRACE AMOUNTS OF SILVER

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Summary—Silver can be extracted from near-neutral aqueous solution into nitrobenzene as the ion-association system formed between its 1,10-phenanthroline complex and bromopyrogallol red. In the presence of EDTA, mercury(II) and bromide ions as masking agents, the extraction system is highly selective. Of 42 ions examined, only thiosulphate and large amounts of gold interfere. The colour system is very sensitive ($\epsilon = 32{,}000$). Also, it can readily be applied to the indirect determination of concentrations of cyanide down to 0·026 ppm by determination of an added excess of silver.

THE few extraction systems that exist for silver are, in the main, dependent on chelation and are, as a consequence, somewhat unselective in action. Notable exceptions are the ion-association systems developed by Betteridge and West[1] and by Ziegler *et al.*[2] However, even these systems have some limitations, especially with anions which form strong silver complexes. In addition, some cations interfere,[1] among the more prominent being mercury(II).

In our examination of the very sensitive and selective silver/1,10-phenanthroline/bromopyrogallol red method,[3] it was noted that very large amounts of anions completely prevented the development of the colour system. Even nitrate, when present in greater than a 1000-fold mole excess over silver, completely prevented all colour development. This is, of course, in keeping with the behaviour of ion association systems of which the above is an example. In addition, with large amounts of silver ($10^{-4}M$ solutions) there is danger of precipitation. Thus, although this reaction is extremely sensitive in aqueous solution ($\epsilon = 51{,}000$), its usefulness is limited by interference from anions and it cannot be used for the determination of amounts of silver larger than 10 μg.

With these restrictions in mind, the possibilities of extracting the blue ternary complex, produced between silver, 1,10-phenanthroline and bromopyrogallol red, from near-neutral solution were investigated.

Water-immiscible solvents, such as ether, benzene, carbon tetrachloride, chloroform, methyl isobutyl ketone, amines, higher alcohols, *etc.*, all caused the blue complex to collect at the interface of the two phases. In addition, water-miscible solvents prevented or completely destroyed the colour. Only nitrobenzene was found to be capable of extracting the complex. In this medium the maximum absorption peak was at 590 mμ (*cf.* 635 mμ in aqueous solution) when compared with a blank of distilled water or nitrobenzene. Although the colour slowly faded to brown after several days, there was no sign of any precipitation at any time. The colour

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could also be developed directly in the nitrobenzene phase by first extracting an aqueous solution of silver nitrate and 1,10-phenanthroline at pH *ca.* 7 with nitrobenzene, followed by an equilibration with an aqueous solution of bromopyrogallol red in 1% ammonium acetate. The dyestuff itself is not extracted by nitrobenzene.

Procedures were subsequently developed along these lines for the determination of 10-50 μg of silver directly in the nitrobenzene phase. The molar extinction coefficient was calculated to be 32,000, which is equal to that of the standard dithizone and *p*-dimethylaminobenzalrhodanine methods. In addition, amounts of silver down to 1 μg, can be determined with but slight alteration in the recommended procedure. Small concentrations of silver can be determined by using the extraction system as a means of concentration.

The major difficulty encountered in this investigation was the slowness of the phase separation, following the final extraction with an aqueous solution of bromopyrogallol red. An ice-water treatment of the separating funnels was unsuccessful and the addition of a very large excess of electrolyte merely destroyed the colour of the final complex in the nitrobenzene phase.

The turbidity of the organic phase could be removed, without prolonged standing, by running it into a beaker containing a few pellets (*ca.* 5) of sodium hydroxide. Upon swirling, the turbidity disappeared in about 1 min. However, under these conditions the stability of the solutions was somewhat reduced and the absorbance measurements had to be made within 0·5 hr of this treatment. Other drying agents, such as calcium chloride, oxide and sulphate, *etc.*, merely adsorbed the blue complex, *cf.* however Note 1.

The effect of the 1,10-phenanthroline concentration on the efficiency of the extraction system was determined. It was concluded that, provided a 5-fold mole excess over silver was present, there was no significant increase or decrease in the expected absorbances. The effect of EDTA was similarly investigated, but once again it had no pronounced effect, even with amounts such as 10 ml of a $10^{-1}M$ solution. Furthermore, the order of addition of reagents was found to be equally unimportant.

Interferences

Because of the anionic interference in aqueous solution, this examination was restricted, in the first instance, to about a 1000-fold g ion excess over silver of the following anions: sulphate, phosphate, carbonate, chloride, bromide, iodide, fluoride, cyanide, thiocyanate, chlorate, thiosulphate, nitrate, acetate, oxalate and citrate. Provided that the aqueous phase is removed after the initial extraction of the silver/1,10-phenanthroline with nitrobenzene, and before the final extraction with an aqueous solution of bromopyrogallol red, only cyanide, thiocyanate, iodide and thiosulphate interfere. With the aid of a *double masking action* with mercury(II) ions, only thiosulphate continued to interfere. A sufficient excess of mercury(II) ions is added to the solution containing silver and 1,10-phenanthroline to complex cyanide, thiocyanate and iodide. Excess EDTA is then added to complex the excess mercury(II). Under these conditions only silver and 1,10-phenanthroline are extracted and the colour can be developed in the usual way.

Only mercury(II) and copper(II), of those cations previously investigated[3] and found not to interfere in aqueous solution in the presence of excess EDTA, were re-investigated in the extraction procedure. Neither was, however, found to interfere in the recommended procedure, which incorporates, once again, the use of EDTA as a general masking agent.

The cation examination was confined primarily to those ions which were found to interfere in aqueous solution, *i.e.*, niobium(V), gold(III), thorium(IV) and uranium(VI).[3] To these antimony(V) was added because it had been found to give, with bromopyrogallol red, a blue coloured complex, which was stable to EDTA. Under those conditions outlined in the recommended procedure only gold(III) continued to interfere. In addition, it was now unnecessary to add further masking agents, such as hydrogen peroxide or fluoride.

Gold(III), when present in a 5-fold excess over silver, no longer interfered if a sufficient amount of bromide ions was added to form the $AuBr_4^-$ complex before the initial extraction. Alternatively, the extraction can be carried out from ammoniacal solution at pH 10. The ammine complex of gold now prevents its extraction, but a decrease in sensitivity (*ca.* 4-fold) is obtained because of the less efficient extraction of silver/1,10-phenanthroline at this elevated pH.

Thus, the proposed extraction is completely free from the interference of the 26 cations and 14 anions examined, *viz.*, aluminium(III), ammonium, antimony(V), barium(II), bismuth(III), cadmium(II), calcium(II), cerium(III), chromium(III), cobalt(II), copper(II), iron(II), iron(III), lanthanum(III), lead(II), magnesium(II), manganese(II), mercury(II), niobium(V), nickel(II), palladium(II), thallium(I), thorium(IV), titanium(IV), uranium(VI), zinc(II) and acetate, bromide, carbonate, chloride, chlorate, citrate, cyanide, fluoride, iodide, nitrate, phosphate, sulphate, tartrate and thiocyanate. Only thiosulphate and large amounts of gold(III) caused interference.

EXPERIMENTAL

Reagents

$10^{-4}M$ *Silver nitrate solution.* Prepare by dilution of standard $10^{-1}M$ silver nitrate solution.

$10^{-3}M$ *1,10-Phenanthroline solution.* Dissolve 49·56 mg of analytical reagent grade 1,10-phenanthroline in distilled water and dilute to 250 ml.

20% *Ammonium acetate solution.* Dissolve 20 g of analytical reagent grade ammonium acetate in distilled water and dilute to 100 ml.

$10^{-4}M$ *Bromopyrogallol red solution.* Dissolve 13·96 mg of bromopyrogallol red plus 2·5 g of analytical reagent grade ammonium acetate in distilled water and dilute to 250 ml. This solution should be discarded after 5 days.

$10^{-1}M$ *EDTA solution.* Dissolve 3·7225 g of the analytical reagent grade disodium salt in distilled water and dilute to 100 ml.

$1M$ *Sodium nitrate solution.* Dissolve 8·5 g of analytical reagent grade sodium nitrate in distilled water and dilute to 100 ml.

Nitrobenzene, Reagent grade

Sodium hydroxide, Reagent grade pellets

Apparatus

A Unicam SP 600 spectrophotometer was used for the absorbance measurements.

Procedure

Calibration curve. Pipette 1–5 ml of $10^{-4}M$ silver nitrate solution, 1 ml of 20% ammonium acetate solution, 5 ml of $10^{-3}M$ 1,10-phenanthroline solution, 1 ml of $10^{-1}M$ EDTA solution and 1 ml of $1M$ sodium nitrate solution into 100-ml separating funnels. Add sufficient distilled water to give a constant volume of solution in each funnel, then add 20 ml of nitrobenzene and shake by continuous inversion for 1 min. Allow about 10 min for the layers to separate, then transfer the lower organic layers to different 100-ml separating funnels and add to the latter 25 ml of $10^{-4}M$ bromopyrogallol red solution. Again shake by continuous inversion for 1 min and allow about 30 min for the layers to separate. Run the lower nitrobenzene layers into 100-ml beakers, each containing about 5 pellets of sodium hydroxide (*Note 1*) and swirl each beaker until all cloudiness disappears (*ca.* 1 min). Finally, transfer the solutions to 1-cm cuvettes and, as soon as possible (within 0·5 hr), measure the absorbance at 590 mμ against a blank carried through the same procedure, but containing no silver:

$$1 \text{ ml of } 10^{-4}M \text{ AgNO}_3 \equiv 10{\cdot}788\ \mu\text{g of Ag.}$$

The graph of absorbance *vs.* micrograms of silver is a straight line from 10 to 50 μg of silver and passes through the origin.

Determinations. Take an aliquot of the silver test solution, containing between 10 and 50 μg of silver, and add sufficient EDTA to complex all those cations present which form an EDTA complex. If gold is present (<250 μg), add, in addition, sufficient bromide ion to form the $AuBr_4^-$ complex. If cyanide, thiocyanate or iodide is present, add sufficient mercury(II) ions to complex these anions followed by sufficient EDTA to complex any excess mercury(II). Add 1 ml of 20% ammonium acetate solution, *etc.*, and proceed as under *Calibration Curve.* Only thiosulphate interferes in this determination.

The determination of smaller amounts of silver can be carried out in a similar manner by using 4-cm cuvettes (for 1–10 μg of silver) or by using the extraction system as a means of concentration.

DISCUSSION

The proposed method is, in most respects, superior to the existing spectrophotometric procedures for the determination of silver. It is simple and quick in operation; there is no need for a special purification of reagents and the usual disadvantages associated with the dithizone and rhodanine methods are, therefore, eliminated. The method is equally as sensitive ($\epsilon = 32{,}000$) as the hitherto most sensitive silver reagent *p*-dimethylaminobenzalrhodanine. In addition, because of the use of masking agents and the selectivity of the nitrobenzene extraction system, only thiosulphate was found to interfere. The solution colours are stable for 0·5 hr after complete colour development and, provided the bromopyrogallol red reagent solution is not kept for longer than about 5 days, reproducible results can be obtained. With large amounts of silver (10–50 μg) there is no danger of precipitation, and smaller amounts of silver can readily be determined with the minimum of alteration in the recommended procedure.

Furthermore, the method can be readily applied to the indirect determination of trace amounts of cyanide by determination of an added excess of silver. Thus, by employing 10 ml of a 10^{-4} *M* silver nitrate solution and extracting into 40 ml of nitrobenzene in the recommended procedure, 2·602–13·01 μg of cyanide (1–5 ml of 10^{-4} *M* potassium cyanide solution) can be determined. Smaller concentrations of cyanide can be determined by using the extraction system as a means of concentration. Cyanide, in the range 0·026–2·6 ppm, has been determined in this way. The advantages of this method are that, of the common anions, only thiocyanate, iodide and thiosulphate interfere; in addition, only those cations which form a more stable complex with cyanide than silver (*e.g.*, Hg^{2+}), will interfere.

The complex produced in aqueous solution between silver, 1,10-phenanthroline and bromopyrogallol red is an ion-association system, $([\text{Phen-Ag-Phen}]^+)_2 \cdot \text{BPR}^{2-}$. This accounts for the selectivity and sensitivity of the method and for the instability towards anions in aqueous solution. However, there is still some doubt as to the mechanism of the extraction into nitrobenzene. Preliminary experiments suggest the existence of a differently constituted species in this solvent, probably $[\text{Phen-Ag-Phen}]^+ \cdot \text{BPR}^{2-}$, which would account for the decrease in the value of the molecular extinction coefficient and for the shift in wavelength of maximum absorption. Work is now proceeding on this aspect and on the possibility of using chromogens which do not contain chelating groups. Ligand bases other than 1,10-phenanthroline are also being investigated.

Note 1. The sodium hydroxide is the source of instability of the colour system, which is otherwise as stable as that of the aqueous one.[3] We have found more recently that the use of sodium hydroxide is unnecessary. Effective clarification of the nitrobenzene extract can be obtained by swirling a portion of it in a clean dry beaker before transference to the cuvette.

Zusammenfassung—Silber kann aus fast neutraler wäßriger Lösung als Ionenassoziat zwischen seinem 1,10-Phenanthrolinkomplex und Brompyrogallolrot mit Nitrobenzol extrahiert werden. In Gegenwart von EDTA, Quecksilber(II) und Bromid zur Maskierung ist das Extraktionssystem hochselektiv. Unter 42 untersuchten Ionen störten nur Thiosulfat und große Mengen Gold. Die Farbreaktion ist sehr empfindlich ($\epsilon = 32\,000$). In gleicher Weise kann die Methode zur indirekten Bestimmung von Cyanid bis herunter zu 0,026 ppm verwendet werden durch Bestimmung eines zugesetzten Silberüberschusses.

Résumé—On peut extraire l'argent au nitrobenzène, à partir de solutions aqueuses voisines de la neutralité, à l'état de système d'association ionique formé entre son complexe 1,10-phénanthrolinique et le rouge de bromopyrogallol. En présence d'EDTA, et d'ions mercure (II) et bromure comme agents dissimulants, le système d'extraction est hautement sélectif. Parmi 42 ions examinés, seuls l'hyposulfite et de fortes quantités d'or interfèrent. Le système coloré est très sensible ($E = 32\,000$). On peut aussi appliquer aisément cette méthode au dosage indirect de concentrations en cyanure aussi faibles que 0,026 p.p.m. par dosage d'un excès d'argent ajouté.

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DETERMINATION OF BERYLLIUM BY MEANS OF HEXAMMINECOBALT(III) CARBONATOBERYLLATE—I

COMPOSITION OF THE PRECIPITATE AND ITS SUITABILITY AS A WEIGHING FORM FOR BERYLLIUM

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Summary—The precipitate obtained when hexamminecobalt(III) chloride is added to a solution of beryllium in excess ammonium carbonate has been analysed and its behaviour under different humidity conditions examined. The composition is that of hexamminecobalt(III) hexacarbonato-oxo-tetraberyllate $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot xH_2O$, as suggested by Sen Gupta, rather than that of Pirtea $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$. x depends on the humidity of conditioning, varying between 10·8 and 11·1 at relative humidities between 32 and 80%. Drying the precipitate *in vacuo* over anhydrous magnesium perchlorate or phosphorus pentoxide results in 3 molecules of water being retained. The compound as normally precipitated may be a mixture of the deca- and dodecahydrates that Sen Gupta prepared. After conditioning at a definite humidity and if an empirical factor is used, the precipitate may be suitable as a gravimetric form for determining beryllium where precision requirements are not too exacting.

Over the past few years the development of beryllium metallurgy has resulted in the production of increasingly pure metal and consequently in heavier demands on the analytical chemist. The purest metal now available has a total impurity content of not more than 0·05%, most of which is oxygen, and it is desirable to have a highly accurate and precise beryllium assay method to supplement other analytical information.

The accurate determination of beryllium is a matter of some difficulty because the element does not readily form complexes or insoluble compounds of definite stoichiometric composition. The oxide has, perhaps, been most used for the gravimetric determination of beryllium, the hydroxide being precipitated in the presence of ethylenediaminetetra-acetate (EDTA) ion, which complexes a wide range of other cations. Unfortunately, this is not completely successful in preventing coprecipitation of impurities and it is usually necessary to carry out a spectrographic analysis of the oxide to enable suitable corrections to be made. This method also suffers from the usual difficulties associated with the high temperature ignition and weighing of a hygroscopic oxide. The determination as pyrophosphate suffers from similar disadvantages.

A number of organic precipitants have been proposed for the determination of beryllium, including 8-hydroxyquinaldine, β-hydroxy-α-naphthaldehyde and dimethylhexandione, but none of the resulting procedures is of a sufficiently high order of precision for the present purpose.

A method based on the potentiometric titration of the hydroxyl ion liberated in the reaction

$$Be(OH)_2 + 4F^- \rightarrow BeF_4^{2-} + 2OH^-$$

has been described by McClure and Banks[1] and has been used quite widely. This is an empirical procedure and the acid titrant must be standardised against beryllium. It was used routinely in this Establishment for some time, for moderately pure beryllium metal, giving results reproducible to 0·1–0·2%. However, on occasions the method broke down completely and a more reliable procedure was required.

A number of papers by Pirtea[2–4] and coworkers describe a gravimetric method for determining beryllium in which the element is precipitated as a hexamminecobalt(III) compound of a carbonatoberyllate anion. Good results were obtained with quantities of beryllium between 0·9 and 72 mg, the reproducibility being about 0·1% of the beryllium added at the higher levels; a micro-adaptation was shown to be satisfactory for quantities of beryllium between 70 and 350 μg. In this procedure the beryllium solution is neutralised and a large excess of ammonium carbonate added, forming the basic carbonatoberyllate anion. Any precipitated beryllium hydroxide or carbonate dissolves fairly readily in ammonium carbonate and a clear solution is obtained. Excess saturated hexamminecobalt(III) chloride is then added. After standing for some time the precipitate is collected on a sintered glass crucible, washed successively with 0·2% hexamminecobalt(III) chloride solution, 60% alcohol, absolute alcohol and ether. The precipitate is first dried by suction, then left in a vacuum desiccator for 15 min and weighed. The method was shown to be highly selective for beryllium if carried out in the presence of a suitable complexing agent, such as tartrate or EDTA, to prevent the precipitation of metals giving insoluble hydroxides or carbonates.

The above method appeared to be the most promising of available procedures from which a highly precise beryllium assay method might be developed and it was decided to investigate it further. The composition assigned to the complex by Pirtea disagrees with the results of other workers on carbonatoberyllates, although these are not entirely consistent with each other, as is shown below.

Compounds of basic beryllium carbonate were first prepared in 1855 by Debray,[5] who dissolved beryllium hydroxide in aqueous potassium carbonate solution. From this solution he isolated the potassium salt to which he assigned the formula $3K_2Be(CO_3)_2 \cdot Be(OH)_2$; he and Klatzo[5] prepared the corresponding ammonium salt. More recently, Sen Gupta[6] dissolved beryllium hydroxide in aqueous potassium bicarbonate and from the resulting solution he isolated a hygroscopic compound which he considers to be a hydrated form of $K_6[Be_4O(CO_3)_6]$; he similarly obtained the corresponding sodium salt. Ignoring the water content, Debray's and Sen Gupta's products are identical in composition. The formula proposed by Sen Gupta contains the anion $[Be_4O(CO_3)_6]^{6-}$, which has the typical basic beryllium carboxylate structure as found in the basic acetate $Be_4O(CH_3COO)_6$.

In contrast with the above observations, Humpidge,[5] in 1886, prepared an ammonium carbonatoberyllate whose formula he gave as $2(NH_4)_2Be(CO_3)_2 \cdot Be(OH)_2$. As regards the hexamminecobalt(III) compound, Pirtea gives it the formula $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3] \cdot 3H_2O$, whereas Sen Gupta considers it to have the same anion as the other salts and writes the formula as $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]$. Sen Gupta finds it to contain 10 or 12 molecules of water "according to the amounts of ammonium carbonate or alkali bicarbonate utilised for complexing beryllium". The $10H_2O$ compound gives tetrahedral and octahedral crystals, while the crystals of the $12H_2O$ are said to be feather-like. He states that the latter can be used for the gravimetric determination of beryllium, but gives no details as to how each hydrate can be produced or how he dried his precipitates.

The formulae given by Sen Gupta for his compounds are all supported by analytical results for N, Be, C and H. However, no such evidence is given by Pirtea and it is difficult to see on what grounds he arrives at his rather odd formula. The only statement made in its justification, literally translated from the Rumanian, is as follows: "Given the high molecular weight of the compound obtained, 440, corresponding to an empirical formula $[(H_2O)_2Be_2(CO_3)_2(OH)_3][Co(NH_3)_6]\cdot 3H_2O$ and the small atomic weight of beryllium, 9·02, beryllium enters into this compound in the proportion of only 4·10%." The experimental results obtained by Pirtea, using 4·10% as the beryllium content of the precipitate, appear to be good, in-so-far as the weight of beryllium found agrees with the amount added, but here the paper is obscure in another respect. It appears that the beryllium was added as a standard solution of $Be(NO_3)_2\cdot 4H_2O$ but it is not stated how the solution was standardised.

From the foregoing it was evident that it would first be necessary to establish the composition of the precipitate and experiments for this purpose are described below.

EXPERIMENTAL

Preliminary experiments showed that vacuum desiccation of hexamminecobalt(III) carbonatoberyllate over anhydrous magnesium perchlorate or phosphorus pentoxide resulted in continuous weight loss over a period of a day or two before constant weight was reached. The short drying period of 15 min in a vacuum desiccator as recommended by Pirtea could not, therefore, be regarded as a satisfactory procedure. Experiments were therefore performed to determine whether a suitable conditioning procedure at a definite humidity would give a product of sufficiently stable composition for weighing.

Stability of Compound at Various Humidities

Reagents

Standard beryllium solution (about 2% by weight). Prepared by dissolving beryllium metal flake of 99·8% purity (based on impurity analysis) in hydrochloric acid in a tared flask, diluting and weighing. Portions of the solution were weighed out as required from a polythene ampoule drawn out to a fine jet.

25% *Ammonium carbonate solution (containing EDTA).* 250 g of ammonium carbonate and 4 g of disodium ethylenediaminetetra-acetate were dissolved by stirring with 500 ml of water containing 120 ml of concentrated aqueous ammonia, and the solution diluted to 1 litre.

Hexamminecobalt(III) chloride. 5% aqueous solution

Wash solutions. 0·2% aqueous hexamminecobalt(III) chloride
60% v/v ethanol and water

Procedure

A weighed portion of beryllium solution was diluted to about 25 ml, 1*M* aqueous ammonia added until a permanent precipitate was formed and the latter dissolved by the addition of 1*M* hydrochloric acid. 20 ml of ammonium carbonate solution were added and the solution heated to about 60° for a few minutes until it became completely clear. An excess (20–50%) of 5% hexamminecobalt(III) chloride solution was then added and the solution allowed to cool to room temperature. The precipitate was collected on a tared X4 sintered glass crucible and washed successively with 0·2% hexamminecobalt(III) chloride solution and 60% v/v ethanol. It was then dried by suction (about 15–20 min). Washing with absolute ethanol was avoided to prevent possible dehydration of the compound.

The crucible and contents were weighed and transferred to a desiccator in which an atmosphere of controlled humidity was maintained. The humidifying agents used were moistened crystals of ammonium chloride (about 80% R.H. at 20°), magnesium nitrate (about 55% R.H. at 20°) and calcium chloride (about 32% R.H. at 20°). When constant in weight the sample was transferred to a vacuum desiccator containing anhydrous magnesium perchlorate or, in one experiment, phosphorus pentoxide.

Constant weight, reproducible to about 0·03%, was reached in 10–20 hr at relative humidities of 30–80%. However, dehydration took much longer and the reproducibility was only about 0·3% in these experiments because the desiccated material was very hygroscopic.

The results are shown in Table I.

TABLE I.—EFFECT OF HUMIDITY ON HEXAMMINECOBALT(III) CARBONATOBERYLLATE

Experiment no.		1	2		3		4		5
Weight (*g*) after exposure for 24 hr at:									
80% R.H.		0·8285							
55% R.H.			0·8685						
32% R.H.		0·8236	0·8655		1·2303		0·5213		0·6216
	Hr			Hr		Hr		Hr	
Weight (*g*) after drying *in vacuo* over magnesium perchlorate	2	0·7226	0·7588	20	1·1382	15	0·4466	7	0·5437[a]
	67	0·7005	0·7356	69	1·0472	22	0·4481	72	0·5344[a]
	70	0·7029	0·7389	72	1·0507	84	0·4440	104	0·5347[a]
						116	0·4454	170	0·5337[a]
Weight relative to that at 32% R.H. after exposure to:									
80% R.H.		1·0059							
55% R.H.			1·0035						
magnesium perchlorate[b]		0·851	0·850		0·851		0·852		0·859[a]

[a] Dried over phosphorus pentoxide.

[b] Ratios were calculated from the minimum weights observed.

Analysis for Elementary Constituents

Early experiments showed that conditioning at 30–80% R.H. gave a product sufficiently stable to handle in the ordinary laboratory atmosphere without the occurrence of sudden weight changes. Further experiments were carried out in which the complex was conditioned for 24 hr at 32% R.H., then analysed for cobalt, carbon, hydrogen and nitrogen. Four precipitations were carried out and cobalt determined on all four precipitates by the method to be described in Part II. Duplicate determinations of carbon, hydrogen and nitrogen by micro-combustion were made on two of the precipitates. The beryllium content of the precipitate was calculated from the known amounts added on the assumption of complete precipitation.

These results are shown in Table II.

DISCUSSION

It is clear, from the atomic ratios of carbon to the other elements shown in Table II, that the precipitate has the composition stated by Sen Gupta and not that of Pirtea. The compound should, therefore, be termed hexamminecobalt(III) hexacarbonato-oxo-tetraberyllate and has the formula $[\mathrm{Co(NH_3)_6}]_2[\mathrm{Be_4O(CO_3)_6}]\cdot x\mathrm{H_2O}$. The value of x may be calculated from the cobalt content, which was the most accurate of the determinations carried out. The mean value of the cobalt content of the compound conditioned at 32% R.H. was 12·696 ± 0·003%, corresponding to a molecular weight of 928·4 and giving x the value of 10·8. From the results in Table I, x has the value of 11·0 and 11·1 for the material conditioned at 55% and 80% R.H., respectively. 3·0 molecules of water are retained by the precipitate after drying *in vacuo* over magnesium perchlorate. In view of Sen Gupta's identification of the deca- and dodecahydrates it is possible that these species are of very similar

TABLE II.—COMPOSITION OF HEXAMMINECOBALT(III) CARBONATOBERYLLATE

Experiment no.	Be taken, g	Ppt. at 32% R.H., g	Composition, % *by weight*					Atomic ratios			
			Co	Be	C	N	H	N/C	C/Be	C/Co	Be/Co
6	0·02433	0·6237	12·695	3·901	—	—	—	—	—	—	2·009
7	0·01702	0·4367	12·693	3·897	—	—	—	—	—	—	2·008
8	0·04924	1·2628	12·691	3·899	8·0 8·1	18·8 18·9	6·2 6·2	2·01	1·54	3·11	2·009
9	0·05120	1·3154	12·704	3·892	7·7 7·8	18·6 18·8	6·4 6·2	2·07	1·49	2·99	2·003
$[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 10H_2O$			12·889	3·942	7·88	18·38	6·17	2·00	1·50	3·00	2·000
$[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 12H_2O$			12·400	3·793	7·58	17·68	6·36	2·00	1·50	3·00	2·000
$[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$			13·386	4·094	5·46	19·09	7·10	3·00	1·00	2·00	2·000

stability and that the precipitates normally obtained are mixtures of the two. It is difficult to account for the continuous change in composition between 32 and 80% R.H. that we observed, but equilibrium is certainly reached quite rapidly at any humidity in the range. The loss in weight *in vacuo* over magnesium perchlorate also took place rapidly in the initial stages, and in Experiments 1 and 2 over 80% of the total water lost came off in the first 2 hr. Drying the precipitate in a vacuum desiccator for 15 min as recommended by Pirtea would, therefore, be expected to give a large loss in weight and a product of variable composition.

Since completing the above work we have seen the paper of Vinogradov[7] *et al.* on the same subject. They used Pirtea's method for precipitating beryllium and after determining the cobalt, carbonate and water contents of the precipitate, also concluded that it has the Sen Gupta formula. However, they find the beryllium content to be 3·95%, corresponding to 10 molecules of water. Because they followed Pirtea it is presumed that they also dried the precipitate for 15 min *in vacuo* over an unspecified desiccant. Because Pirtea and Vinogradov obtained results of reasonable reproducibility it is presumed that whatever desiccant was used was relatively slow in action. However, even in this case, the system cannot have been in equilibrium and the compound must have been losing weight continuously, if slowly. Vinogradov also measured the rate of decomposition of the compound on heating. He showed that it begins to lose weight at 30° and decomposition proceeds rapidly up to 60°. After a short halt there is another sharp increase in the decomposition rate at 75–85°. The results were rather variable and inconclusive, but about half of the water was lost on drying for 2 hr at 60°.

The rather variable and non-stoichiometric water content of the precipitate renders it unsuitable for the gravimetric determination of beryllium for work of the highest precision. However, as reasonably good reproducibility of composition is attainable by conditioning at a definite humidity it is considered that the method, used empirically, could find application in circumstances where a precision of 0·1–0·2% is adequate. The beryllium content of the precipitate conditioned at 32% R.H. is 3·883%. It should be noted that precipitation conditions in our experiments were not quite optimum. From the Be/Co ratios in Table II it may be calculated that only 99·5–99·8% of the beryllium was precipitated and this is attributed to insufficient dilution of the solution after adding the hexamminecobalt(III) chloride. This point will be dealt with in Part II in which a highly precise method for determining beryllium will be described, based on the determination of the cobalt in the hexamminecobalt(III) hexacarbonato-oxo-tetraberyllate precipitate.

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Zusammenfassung—Der beim Zusatz von Hexamminkobalt(III)-chlorid zu einer Lösung von Beryllium in überschüssigem Ammoniumcarbonat entstehende Niederschlag wurde analysiert und sein Verhalten bei verschiedenen Feuchtigkeiten untersucht. Die Zusammensetzung entspricht Hexamminkobalt(III)-hexacarbonato-oxo-tetraberyllat $[Co(NH_3)_6]_2[Be_4O(CO_3)_6].xH_2O$, wie von Sen Gupta vorgeschlagen, besser als der Formel von Pirtea

$$[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3\ H_2O$$

x hängt von der Feuchtigkeit bei der Aufbewahrung ab, es variiert bei relativen Feuchtigkeiten von 32 bis 80% zwischen 10,8 und 11,1. Beim Trocknen im Vakuum über wasserfreiem Magnesiumperchlorat oder Phosphorpentoxyd werden 3 Moleküle Wasser zurückgehalten. Die normalerweise gefällte Verbindung ist vielleicht eine Mischung der von Sen Gupta hergestellten Deka- und Dodekahydrate. Nach Aufbewahrung bei einer definierten Feuchtigkeit und bei Gebrauch eines empirischen Faktors kann sich der Niederschlag als Wägeform bei der Beryllium-bestimmung eignen, wenn die Genauigkeitsansprüche nicht zu streng sind.

Résumé—On a analysé le précipité obtenu par addition de chlorure de cobaltihexammine à une solution de beryllium dans un excès de carbonate d'ammonium, et étudié son comportement dans différentes conditions d'humidité. La composition est celle de l'hexacarbonate-oxo-tétraberyllate de cobaltihexammine $[Co(NH_3)_6]_2[Be_4O(CO_3)_6],xH_2O$, ainsi que l'a suggéré Sen Gupta, plutôt que celle de Pirtea $[Co(NH_3)_6][(H_2O_2)Be_2(CO_3)_2(OH)_3],3H_2O$. x dépend de l'humidité ambiante, variant entre 10,8 et 11,1 pour des humidités relatives comprises entre 32 et 80%. Après séchage sous vide sur perchlorate de magnésium anhydre ou sur anhydride phosphorique, 3 molécules d'eau sont retenues. Le composé normalement précipité peut être un mélange des déca- et dodécahydrates que Sen Gupta a préparés. Après traitement sous une humidité définie, et par emploi d'un facteur empirique, le précipité peut convenir au dosage gravimétrique du béryllium, lorsque les exigences quant à la précision ne sont pas trop grandes.

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PRECIPITATION OF COPPER 8-HYDROXYQUINALDATE FROM HOMOGENEOUS SOLUTION

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Summary—Copper can be precipitated quantitatively, over a wide range of pH, by 8-hydroxyquinaldine produced from the hydrolysis of 8-acetoxyquinaldine. The copper 8-hydroxyquinaldate can be weighed as either the monohydrate or the anhydrous dichelate. Differences in the appropriate pH conditions, between the PFHS and conventional precipitation methods, and between thorium and copper precipitations from homogeneous solution, are accounted for.

ALTHOUGH precipitation from homogeneous solution (PFHS) has been extensively investigated and used for about twenty-five years, the generation of organic precipitants *in situ* received little attention until three or four years ago. Interest in this field is increasing, as a recent survey[1] of the literature shows. Since that review, studies[2,3] have revealed advantages, for the precipitation of zinc and of indium, of 8-acetoxyquinaldine as a source reagent for the precipitant 8-hydroxyquinaldine.

A study[4] of the precipitation of thorium 8-hydroxyquinaldate [thorium 2-methyloxinate, $Th(C_{10}H_8ON)_4$] *via* the hydrolysis of 8-acetoxyquinaldine disclosed a disadvantage of the PFHS method: the pH conditions for the quantitative precipitation of the pure chelate can be much more restrictive than in the conventional method. It was anticipated that, with regard to the pH conditions for successful precipitation, the difference between the conventional and PFHS methods would be much less with copper than with thorium. The present work demonstrates that this is so, and that copper can be determined with high precision and accuracy through the agency of 8-acetoxyquinaldine.

EXPERIMENTAL

Reagents and procedures

Copper(II) solution: Copper foil (AnalaR) was dissolved in nitric acid, and the solution was diluted with water to a concentration ~1·0 mg of Cu/ml. Standardisation was done iodometrically, using procedures recommended by Hammock and Swift.[5]

8-Acetoxyquinaldine (8-AQD): The sources of, and method of storing, this reagent were the same as in an earlier study.[4] The infrared spectra (in Nujol) of the commercial and synthesised products were the same; in neither was the hydroxyl stretching band at about 3400 cm^{-1} detected. Solutions were made by dissolving in 2·0 ml of glacial acetic acid the amount of 8-AQD required to give 20% or 200% excess of reagent, and diluting with water to 10 ml (100 mg of 8-AQD are equivalent to 15·8 mg of copper, for the 1:2 chelate).

All other chemicals were reagent-grade. Weights and volumetric ware were calibrated. The thermobalance has been described previously.[4]

The pH values of precipitation were determined by measurements on the filtrates at room temperature; the meter was standardised before use by an appropriate buffer solution, and readings of pH >10 were corrected for sodium-ion error.

Precipitation of copper 8-hydroxyquinaldate

Twenty-five ml of copper(II) solution (1 mg/ml) were diluted with water to 225 ml and 10 ml of a freshly prepared solution of 8-AQD (*vide supra*) were added. The pH was adjusted using 1·5–3M aqueous ammonia (or, for precipitations at pH values >10, using 2–5M sodium hydroxide), added drop by drop with vigorous stirring. (To allow for drift during precipitation, the pH was brought to a value higher than that desired after precipitation: about 0·1 unit higher at pH 5; about 1 unit at pH 7.) The solution was warmed for 2 hr at ~80°, filtered (medium porosity frit), and the precipitate washed, using for the transferring and washing about 100 ml of hot water. The precipitate was dried for 2 hr at 105–110° or for 1 hr at 125–130°, cooled over phosphorus pentoxide, and weighed as $Cu(C_{10}H_8ON)_2$.

RESULTS AND DISCUSSION

Character and composition of the precipitate

Precipitation began after some minutes of heating. The delay at pH 5.2 was less than half that at pH 4·0: this is a consequence of a sharp increase in the rate of hydrolysis of 8-AQD with increasing pH in the range 3·0 to 5·5.[6] The precipitate was distinctly crystalline, consisting of large, well-formed, thin, brown plates that were readily washed.

On being heated at 105–130°, the precipitate became dark green. That this reflects the dehydration of $Cu(C_{10}H_8ON)_2{\cdot}H_2O$ was established by the following (all precipitations at pH 4·5–9·5): weights of the brown product, dried at 60° for 16 hr, corresponded to quantitative recovery of the copper as the dichelate monohydrate; weights of the green product, dried for 2 hr at 105–110° or 1 hr at 125–130°, corresponded to quantitative recovery as the anhydrous dichelate; the green compound had a copper content (by ignition) of $16{\cdot}7_1\%$ with an average deviation of $0{\cdot}0_2\%$ (theoretical, for $Cu(C_{10}H_8ON)_2$, 16·73%); and thermogravimetric curves for precipitates previously dried at room temperature for 72 hr showed a break beginning at 102° followed by another plateau from about 130° to 230°, the decrease in weight corresponding to the loss of the hydrate water. (These temperatures are reasonably close to those found by Borrel and Pâris,[7] and we agree that the oxide level is reached at about 600°.)

pH Range for quantitative precipitation

The recommended procedure, even with an excess of reagent of only 20%, permits the quantitative recovery of copper (from solutions of concentration ~90 mg of Cu/litre or $1{\cdot}4 \times 10^{-3}M$) as the dichelate, with high precision, over a wide range of pH. Sixteen determinations in the pH range 4·5–9·5 had an average deviation, from the 100·0% recovery value, of only 0·1%.

The pH range for quantitative precipitation can, of course, be extended by increasing the excess of reagent (Fig. 1). The pH values for both "incipient" and quantitative precipitation of a metal chelate depend on several factors, including the concentration of any complexing anions in the solution; in spite of such differences, our values (pH 3·2 and 4·5 for 20% excess reagent; pH 2·9 and 3·9 for 200% excess) are in good agreement with other results[8,9] obtained using 8-hydroxyquinaldine directly.

No work bearing on the upper limit of pH for the quantitative precipitation of copper 8-hydroxyquinaldate is known to us. With 20% excess reagent, we found that precipitation—calculated as the dichelate—beyond pH 10 began to fall below 100%, decreasing to 94% at pH 13·9. In this same range, the copper contents of the precipitates (dried at 105–130°) rose from $16{\cdot}7_1\%$ (proper for the anhydrous dichelate) to $16{\cdot}8_6\%$. These results indicate that precipitation beyond pH 10 occurs as an hydroxychelate or a mixture of the normal chelate and hydrous copper oxide. Moreover, more than one kind of experiment showed that (regardless of the composition of the precipitate), at least at and beyond pH 12·8, copper was not quantitatively precipitated; this, too, is likely due to hydroxo complexing.

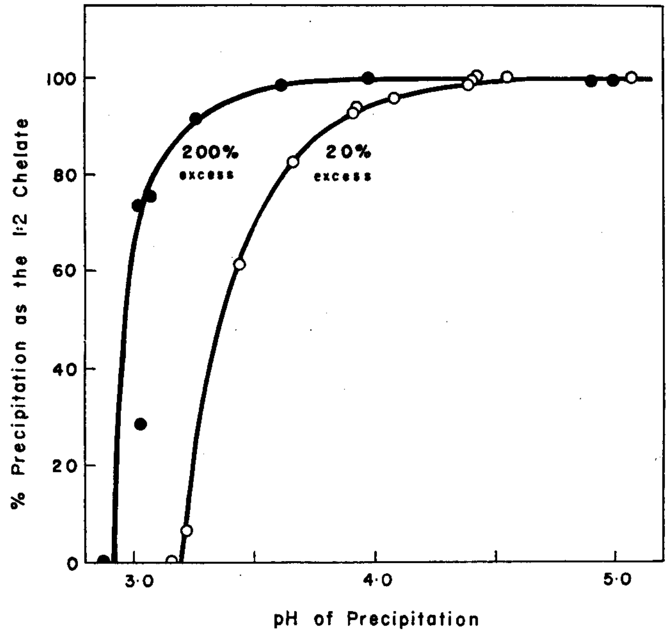

FIG. 1.—Precipitation of copper 8-hydroxyquinaldate from homogeneous solution in relation to pH of precipitation and excess of reagent.
(Copper in original solution = 0·1 mg/ml.)

Comparison of PFHS and conventional methods

With 20% excess reagent, precipitation of copper, by this PFHS method ceased to be quantitative (100·0 ± 0·1%) *as the dichelate* at pH 10; recovery of copper in this form was 99·5% in the pH range 10–12, thereafter decreasing more sharply with increasing pH, to 94% at pH 13·9 as has been mentioned. In contrast, in precipitations in which 8-hydroxyquinaldine was used directly, but which otherwise were comparable, quantitative precipitation of copper as the dichelate was obtained at pH values up to 12.

This wider pH range for successful precipitation using the conventional precipitation method is consistent with what was found with thorium,[4] although the effect is much less pronounced with copper. The differences in the useful pH range of the two methods likely arise from the different concentrations of the chelating quinaldate anion during adjustment of the pH and the consequences of this, as elaborated in the earlier paper.[4] That copper shows this effect in much lesser degree than thorium is to be expected. The effect stems from a competition between hydroxyl-ion and chelating anion for the metal-ion, and thorium-ion is, of course, relatively very prone to hydrolysis. Of the bivalent metal-ions of the first transition period, copper may have the widest pH range for successful precipitation of the 8-hydroxyquinaldate, because of the high stability of copper chelates. Another relevant factor, though, is the intrinsic solubility[10] of the chelate, and the intrinsic solubilities of these metal chelates may differ appreciably. In fact, pronounced differences in the intrinsic solubilities of the 8-hydroxyquinolates of cobalt, copper and zinc have recently been reported[11] and, moreover, the intrinsic solubilities of these chelates do not follow their stability order.

In any event, copper can be quantitatively precipitated as the 8-hydroxyquinaldate over a wide pH range: 6 to 8 or more pH units, depending on the excess of reagent and whether 8-acetoxyquinaldine or 8-hydroxyquinaldine directly is used.

Acknowledgement—We gratefully acknowledge financial support from the National Research Council of Canada.

Zusammenfassung—Kupfer kann quantitativ in einem weiten pH-Bereich mit 8-Hydroxychinaldin gefällt werden, das durch Hydrolyse von 8-Acetoxychinaldin erzeugt wird. Das Kupfer-8-hydroxychinaldinat kann entweder als Monohydrat oder als wasserfreies Dichelat gewogen werden. Unterschiede in den geeigneten pH-Werten zwischen der Fällung aus homogener Lösung und konventionellen Fällungsmethoden und zwischen Thorium- und Kupferfällungen aus homogener Lösung werden berücksichtigt.

Résumé—On peut précipiter quantitativement le cuivre, dans un large domaine de pH, au moyen de 8-hydroxyquinaldine produite par hydrolyse de la 8-acétoxyquinaldine. Le 8-hydroxyquinaldinate de cuivre peut être pesé à l'état de monohydrate ou de dichélate anhydre. On interprète les différences observées, dans des conditions de pH appropriées, entre la méthode de précipitation en milieu homogène et les méthodes de précipitation usuelles, et entre les précipitations du thorium et du cuivre en milieu homogène.

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SPECTROPHOTOMETRIC INVESTIGATION OF THE NATURE AND STABILITY OF SILVER(II) IN ACIDIC SULPHATE MEDIA

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Summary—A spectrophotometric study of silver(II) in sulphuric acid solution indicates the formation of two sulphato complexes, in the range 4–18*M* H_2SO_4, with absorbance peak maxima at 361 and 260 mμ, respectively. In 15*M* H_2SO_4 the molar absorptivity of silver(II) is $3{\cdot}11 \times 10^4$ at 361 mμ. Kinetic studies of the reduction of silver(II) by the solvent suggest a rate-determining step first order in silver(II) and yield a pseudo first-order rate constant of $1{\cdot}9 \times 10^{-1}$ min^{-1}. Further studies as a function of H_2SO_4 concentration show that the specific decomposition rate of the two complexes is identical and that changes in H_2SO_4 concentration only serve to shift the concentration equilibrium between the two complexes.

INTRODUCTION

IN a previous paper[1] we reported preliminary observations concerning the powerful oxidising agent, silver(II), in aqueous solution at low pH values. Silver(II) was found to be complexed even in perchlorate media and to undergo reduction by the solvent at rates proportional to the square of the silver(II) concentration and inversely proportional to the silver(I) concentration with an over-all activation energy of 11·6 kcal. mole^{-1}.

The present paper describes the results of systematic experiments aimed at elucidating the nature of silver(II) in sulphuric acid media and the details of the reduction of such species by the solvent. In particular, we were interested in establishing the effect of sulphate complexation on the stability of silver(II) with regard to its decomposition to silver(I) to learn whether or not the rate determining step of the over-all oxidation-reduction process involves a change in co-ordination number.

Because of uncertainties in the actual nature of solid silver(II)oxide,[2] employed as starting material in our preliminary experiments, we used an electrolytic generation method, similar to that of Davis and Lingane,[3] to prepare homogeneous solutions of silver(II). Previously unknown data on the nature and optical properties of sulphate-silver(II) complexes are reported in detail.

EXPERIMENTAL

Reagents

All solutions were prepared from reagent-grade materials, except where noted, and used without further purification.

Silver(II) oxide. AgO of 98·5% minimum purity was obtained from Handy & Harmon Company, New York, U.S.A., and was weighed as needed.

Silver(II) sulphate. $AgClO_4{\cdot}H_2O$ (G. F. Smith Chemical Co., Columbus, Ohio, U.S.A.) was used to produce silver(II) sulphate complexes in sulphuric acid media by electrolysis. Best results were obtained by making serial dilutions from 0·2400*M* $AgClO_4{\cdot}H_2O$ in 15*M* H_2SO_4 stock solutions to a final concentration of 0·0024*M* in 15*M* H_2SO_4.

Cerium(IV) sulphate. Pipette 10 ml of 0·1021M cerium(IV) sulphate (G. F. Smith Chemical Co.) in 0·5M sulphuric acid solvent and dilute with 15M sulphuric acid solvent to a total volume of 100 ml. Make further serial dilutions of $5 \cdot 0 \times 10^{-3}$, $1 \cdot 0 \times 10^{-3}$, $5 \cdot 0 \times 10^{-4}$, $1 \cdot 0 \times 10^{-4}$, $5 \cdot 0 \times 10^{-5}$, and $1 \cdot 0 \times 10^{-5}M$ in 15M sulphuric acid.

Cerium(III) sulphate. Weigh 0·3250 g of $Ce_2(SO_4)_3 \cdot 8H_2O$ (G. F. Smith Chemical Co.), dissolve in water and dilute with 18M sulphuric acid to a final concentration of $2 \cdot 04 \times 10^{-3}M$ in 15M sulphuric acid.

Apparatus

Spectra. Spectra and decomposition curves were recorded using a Beckman Model DB ultraviolet-visible spectrophotometer equipped with 1·00-cm matched silica cuvettes. Temperature of both the spectrophotometer and electrolysis cells was held at 25·0° ± 0·15° by a Wilkins-Anderson Co. Lo-Temp Bath system. An E. H. Sargent Model SRL recorder was employed for all absorbance measurements.

Electrolysis. The electrolysis current was provided by a Heathkit Model EUW-17 transistorised power supply. The current and voltage were monitored by Simpson Model 269 and 260 meters, respectively. A cylindrical platinum gauze cathode, 1·40 cm by 3·80 cm, and anode, 2·70 cm by 5·10 cm, were employed to provide proper cell geometry. The cathode was isolated from the anode by a glass cylinder 2·50 cm by 6·20 cm, closed at the bottom by either an "A" or a "C" sintered glass frit. The electrodes, isolation cylinder and electrolysis solution were contained in a thermostatted double-walled glass cell.

Procedure

Silver(II) in sulphuric acid solution was obtained both by dissolution of silver(II) oxide and by electrogeneration at constant current from silver(I). Dissolution was carried out by weighing the desired amount of silver(II) oxide into a 125-ml Erlenmeyer flask and adding 25 ml of sulphuric acid solvent. The flask was swirled until all the silver(II) oxide was dissolved and spectra or decomposition curves were recorded in the usual manner, with correction for initial decomposition time effects where necessary.

Electrolytic production of silver(II) complexes in sulphuric acid. Place 70 ml of silver(I) perchlorate in 15M H_2SO_4 into the electrolysis cell and stir vigorously. Adjust the power supply to furnish currents of 87–90 *mA*, which cause the voltage to be greater than the minimum 1·98 *V* needed with the cell used.[8] After rapid initial production of silver(II), a steady-state concentration of silver(II) is reached because the rate of silver(II) decomposition approaches the electrolysis rate. Because silver(I) inhibits the decomposition of silver(II), the steady-state concentration of the latter can be adjusted by changing the initial silver(I) concentration.

Withdraw samples by pipette and record spectra or decomposition curves in the usual manner, correcting for the time elapsed during sample withdrawal and transfer.

Beer's law was checked for the silver(II) complexes in sulphuric acid by allowing silver(I) to oxidise cerium(III) to cerium(IV) and measuring the absorbance of the stable cerium(IV) complex produced. A typical procedure is given for the determination of the molar absorptivity for the silver(II)-sulphate complex in 15M sulphuric acid at 361 mμ. Spectra of cerium(IV) sulphate in 15M sulphuric acid solvent were obtained in the $1 \cdot 0 \times 10^{-2}$–$1 \cdot 0 \times 10^{-5}M$ range, yielding $\epsilon_{380} = 2 \cdot 36 \times 10^3$ and $\epsilon_{360} = 3 \cdot 86 \times 10^3$, respectively.

Electrolytically generate silver(II)-sulphate complexes from 0·0024M silver(I) perchlorate in 15M sulphuric acid. Withdraw aliquots of the electrolysis solution and follow its decomposition as A_λ *vs.* t, at $\lambda = 361$ mμ. When suitable absorbance readings are reached, rapidly empty the cuvette into a beaker containing 10 ml of $2 \cdot 04 \times 10^{-3}M$ cerium(III) sulphate in 15M sulphuric acid, which provides a large excess of cerium(III). After the redox reaction has taken place, record the spectra of the stable cerium(IV) complex formed. Record the spectra of silver(I) perchlorate and cerium(III) sulphate in 15M sulphuric acid and of 15M sulphuric acid so that wavelengths can be chosen where silver(II) will not be interfered with by cerium(IV), cerium(III), silver(I) or sulphuric acid.

Calculate the actual concentrations of silver(II) corresponding to the measured absorbances at the appropriate wavelength from the amount of cerium(IV) produced by oxidation of cerium(III) by silver(II). Finally, plot A_λ (at $\lambda = 361$ mμ) of the silver(II)-sulphate complex (from decomposition curves) *vs.* the calculated silver(II) concentration. Beer's law is obeyed and the molar absorptivity, ϵ_λ, is calculated.

A further test of the applicability of Beer's law can be obtained using silver(II) from silver(II) oxide. Weigh 0·0023–0·0100 g of silver(II) oxide into 125-ml Erlenmeyer flasks. Add 10 ml of $2 \cdot 0 \times 10^{-3}M$ cerium(III) sulphate in 15M sulphuric acid. When all silver(II) has been reduced to silver(I), record the spectra of the cerium(IV) complex produced. Beer's law plots of A_λ [cerium(IV) produced] *vs.* initial concentration of silver oxide are obtained at $\lambda = 460$, 440, 420 and 410 mμ, all producing excellent straight lines.

RESULTS AND DISCUSSION

Spectra of silver(II) as a function of sulphuric acid concentration

Ultraviolet and visible spectra of an initial concentration of 0·0065 g of silver(II)-oxide in 25 ml of sulphuric acid solvent at 25·0° ± 0·15° suggest that two sulphate complexes of silver(II) are predominant in the range 4–18*M* sulphuric acid. One complex predominates in 10–18*M* acid with absorption maxima between 368 and 343 mμ (visible complex); the second complex predominates between 4 and 9*M* acid with absorption maxima between 262 and 245 mμ (ultraviolet complex). An isosbestic point, occurring in 12 and 18*M* acid at 310 mμ, further confirms the fact that significant concentrations of only two complexes in equilibrium are present in these media. Absorbances, at the respective maxima for the two complexes, are equal in 10*M* sulphuric acid.

The visible complex appears only as a shoulder between 339 and 332 mμ on spectra of the ultraviolet complex in the range 4–9*M* sulphuric acid. In the range 0·25–2·5*M* acid no measurable peak of either complex can be distinguished; undissolved particles of silver(II) oxide colour the solutions pale grey initially. Between 4 and 18*M* sulphuric acid, the solutions initially are brownish-yellow and decompose first to pale yellow and then, within a few hours, to water white. The highest absorbance for a given silver(II) concentration is obtained in 15*M* sulphuric acid at 356 mμ and in 5*M* acid at 250 mμ for the visible and ultraviolet complexes, respectively. Spectra of silver(I) perchlorate in sulphuric acid and of sulphuric acid showed no interference at the above wavelengths.

Definite shifts in location of the maxima occur for both complexes and are probably the result of several effects. Spectra taken at various times during the silver(II) decomposition process, but at constant sulphuric acid concentration, show small (3 mμ or less) wavelength shifts; changes in the acid concentration result in substantial changes in peak heights described above. All the above results are summarised in Table I.

Molar absorptivity of silver(II) in sulphuric acid

Beer's law was tested for the visible complex of silver(II) sulphate at 15*M* sulphuric acid at 361 mμ. This acid concentration and wavelength correspond to conditions where the absorbance of the visible complex reaches its maximum value for any given silver(II) concentration. A molar absorptivity of $3{\cdot}11 \times 10^4$ at 361 mμ was calculated for the silver(II) complex. No interference by perchlorate could be noted in the electrogeneration experiments where silver(I) perchlorate was used as a starting material.

Decomposition kinetics of silver(II) complexes in sulphuric acid media

The decomposition of silver(II)-sulphate complexes obtained by dissolution of 0·0050 and 0·0100 g of silver(II) oxide in 15*M* sulphuric acid was followed at 356 mμ (visible complex), 310 mμ (isosbestic point) and 260 mμ (ultraviolet complex), respectively, at 25·0 ± 0·15°. Plots of log absorbance *vs.* time yielded pseudo first-order rate constants of $8{\cdot}44 \times 10^{-2}$, $8{\cdot}79 \times 10^{-2}$ and $9{\cdot}43 \times 10^{-2}$ min^{-1}, respectively. Reliable values are difficult to obtain in such experiments, however, because silver(II) oxide does not instantly dissolve in these media and rate constants are not obtainable from initial slopes. All decomposition experiments were carried out in triplicate.

Silver(II)-sulphate complexes were also obtained by electrogeneration of 0·0024*M* silver(I) perchlorate in 15*M* sulphuric acid and their decomposition followed at 361 mμ at 25·0 ± 0·15°. Good straight lines were obtained for the early portions of log absorbance *vs.* time plots and yielded calculated pseudo first-order rate constants of $1{\cdot}98 \times 10^{-1}$ and $1{\cdot}85 \times 10^{-1}$ min^{-1} for electrolysis currents of 90 *mA* and values of $1{\cdot}85 \times 10^{-1}$ and $1{\cdot}90 \times 10^{-1}$ min^{-1} at 87 *mA*.

Table I.—Spectrophotometric data for silver(II)-sulphate complexes as a function of sulphuric acid concentration

H_2SO_4, *M*	Visible complex maximum, $\lambda(m\mu)$	Absorbance	Ultraviolet complex maximum, $\lambda(m\mu)$	Absorbance
18	368	0·557	260	0·149
17·5	368	0·293	260	0·085
17	364	0·835	260	0·228
16·5	362	0·790	260	0·241
16	362	0·436	260	0·128
15·5	363	0·905	260	0·277
15	356	0·967	260	0·398
14	353	0·758	260	0·309
13	352	0·874	260	0·470
12	346	0·813	260	0·543
11	346	0·973	260	0·805
10	340	0·659	260	0·557
9	339 (shoulder)	0·690	245	0·722
8	334 (shoulder)	0·468	247	0·568
7	334 (shoulder)	0·308	249	0·463
6	332 (shoulder)	0·360	251	0·585
5	334 (shoulder)	0·486	256	0·800
4	334 (shoulder)	0·203	262	0·325
2·5	(360)	0·055	260	0·115
0·5	(360)	0·080	260	0·065
0·25	(360)	0·125	260	0·110

Table II.—Ratio of pseudo-rate constants for the decomposition of silver(II) sulphate complexes

H_2SO_4, *M*	Ratio of rate constants, K	H_2SO_4, *M*	Ratio of rate constants, K
18	1·078	11	0·993
17·5	1·145	10	1·011
17	1·085	9	1·060
16·5	1·047	8	0·997
15	0·906	7	0·794
14	0·911	5	1·016
13	0·936	4	1·001
12	0·997		

In order to establish whether or not the extent of complexation of silver(II) by sulphate has any influence on the kinetics of silver(II) decomposition to silver(I), the absorbance *vs.* time behaviour of the visible and ultraviolet complexes was compared by a ratio method. For each acid concentration (see Table II) complete spectra were recorded at preselected intervals. From these absorbance *vs.* wavelength scans, absorbance *vs*. time data for each of the two complexes could be derived and corrected for any shifts in location of peak maxima and for decomposition during the time required to record each spectrum. A comparison of the specific decomposition rates can be obtained from the slopes, m, of the resulting plots as follows:

$$\frac{A_1 - A_{11}}{t_{11} - t_1} = m_1\,, \qquad \text{for } \lambda_1 \tag{1}$$

$$\frac{A_2 - A_{21}}{t_{21} - t_2} = m_2\,, \qquad \text{for } \lambda_2 \tag{2}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\frac{A_{m(n)} - A_{m(n+1)}}{t_{m(n+1)} - t_{m(n)}} = m_n\,, \qquad \text{for } \lambda_m \tag{3}$$

The standard rate expression, with concentration, C, pseudo-rate constant, k^1, and and reaction order, n^1, is

$$\frac{dC}{dt} = k^1[C]^{n^1} \tag{4}$$

and if $n^1 = 1$, then

$$\frac{dC}{dt} = k^1[C] \tag{5}$$

Substituting absorbance for concentration with $A_1 - A_{11} = \Delta A_{1-11}$, $A_2 - A_{21} = \Delta A_{2-21}, \ldots A_{m(n)} - A_{m(n+1)}$ and $t_{11} - t_1 = \Delta t_{11-1}$, $t_{21} - t_2 = \Delta t_{21-2}, \ldots t_{m(n+1)} - t_{m(n)}$, then combining (3) with (5)

$$\frac{\Delta A_{m(n)-m(n+1)}}{\Delta t_{m(n+1)-m(n)}} = k_m{}^1 A_{m(n+1)} \tag{6}$$

Divide $k_1{}^1$ by $k_2{}^1$ and let $\Delta t_{11-1} = \Delta t_{21-2}$, then

$$\frac{\dfrac{\Delta A_{1-11}}{A_1}}{\dfrac{\Delta A_{2+21}}{A_2}} = \frac{k_1{}^1}{k_2{}^1} = K \tag{7}$$

where K is the ratio of rate constants.

In the system under present consideration, it is experimentally observed that in the ranges of 4–18*M* sulphuric acid at constant initial silver(II) oxide concentration, K, the ratio of pseudo-rate constants, is a constant. Furthermore, the ratio of the pseudo-rate constants for the decomposition of the visible and ultraviolet silver(II)-sulphate complexes is 1·000 ± 0·015 (see Table II). Because the relative concentrations of the two complexes vary widely over the range of acid concentrations studied, one can conclude from the fact that the ratio of rate constants is a constant, that the rate determining step in the silver(II) decomposition is independent of both sulphate and hydrogen ion concentrations. Also, the decomposition reaction must indeed be pseudo first-order, in the range studied, in order to yield a rate constant ratio of unity.

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Zusammenfassung—Eine spektralphotometrische Untersuchung von Silber(II) in schwefelsaurer Lösung zeigt die Bildung zweier Sulfatokomplexe im Bereich von 8–36*n* H_2SO_4 mit Absorptionsmaxima bei 361 mμ und 260 mμ. In 30*n* H_2SO_4 ist der molare Extinktionskoeffizient von Silber(II) 3,11 × 10^4 bei 361 mμ. Kinetische Untersuchungen der Reduktion von Silber(II) durch das Lösungsmittel deuten auf einen geschwindigkeitsbestimmenden Schritt erster Ordnung bezüglich Silber(II) und liefern eine scheinbare Geschwindigkeitskonstante erster Ordnung von 1,9 × 10^{-1} min^{-1}. Weitere Untersuchungen, bei denen die H_2SO_4-Konzentration variiert wurde, zeigen, daß die spezifische Zersetzungsgeschwindigkeit der beiden Komplexe gleich ist und Änderungen in der H_2SO_4-Konzentration nur das Konzentrationsgleichgewicht zwischen den beiden Komplexen verschieben.

Résumé—Une étude spectrophotométrique de l'argent (II) dans l'acide sulfurique montre, dans le domaine 8–36*N* en SO_4H_2, la formation de deux complexes sulfato, avec des pics d'absorption maximale à 361 et 260 mμ respectivement. En SO_4H_2 30*N*, l'absorption molaire de l'argent (II) est de 3,11 × 10^4 à 361 mμ. Des études cinétiques sur la réduction de l'argent (II) par le solvant suggèrent un stade déterminant la vitesse d'ordre un en argent (II), et donnent une constante de vitesse d'ordre pseudo-un de 1,9 × 10^{-1} min^{-1}. Des études ultérieures en fonction de la concentration en SO_4H_2 montrent que la vitesse spécifique de décomposition est identique pour les deux complexes et que les variations dans la concentration de SO_4H_2 servent seulement à déplacer l'équilibre de concentration entre les deux complexes.

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PHOTOMETRIC TITRATIONS—X*

THE EDTA TITRATION OF IRON(III) IN THE PRESENCE OF HIGH CONCENTRATIONS OF BISMUTH

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Summary—In solutions containing a high concentration of ammonium chloride, bismuth is masked as the chloro complex, and iron(III) can be titrated with EDTA to a photometric end-point using sulphosalicylic acid as the indicator. Up to a mole ratio Bi:Fe of about 2,000, good results are obtained. At higher ratios slightly high results are obtained for the iron. The influence of some other metal ions on the titration has been studied.

THE direct chelometric titration of bismuth when present as the chloride is usually difficult, because of the formation of the insoluble oxychloride. It is known that high chloride concentrations prevent the formation of the oxychloride, or redissolve it once it has formed, provided that the pH is lower than about 3. It was thought that addition of high concentrations of chloride might offer a possibility for the direct titration of bismuth because, in such a solution, no precipitate would form. However, under these conditions bismuth gave only a faint colour or no colour at all with several metal indicators tried, and the rate of reaction of bismuth with EDTA was, from all indications, slow. These experimental findings suggested the possibility of using chloride for the "low stability masking" of bismuth. Masking by complex formation is commonly accomplished by employing low concentrations of complexing agents which form fairly stable complexes. However, a few cases are known where high concentrations of complexing agents which form weak complexes are employed. Notable examples are the masking of thorium with sulphate[1] and, recently, of cadmium with iodide.[2] Thus the term "low stability masking" was coined,[3] and investigations indicated that this approach offers further interesting possibilities.

To test this idea an attempt was made to titrate iron in the presence of bismuth, masking the latter by chloride. The stabilities of the EDTA complexes of iron and bismuth are of nearly the same order. Consequently the metals mutually interfere in titration. Although it is not difficult to titrate bismuth in the presence of iron when the latter is masked by reduction to iron(II) with ascorbic acid, the determination of iron in the presence of bismuth is possible only by difference methods. The sum iron + bismuth is titrated in one aliquot and the bismuth is titrated in a second aliquot, after the iron is masked by reduction; the iron is obtained by difference. This procedure yields good results for iron only if the Bi:Fe ratio is close to or below unity. With bismuth present in increasing excess, the results for iron rapidly become less accurate.

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* Part IX: *Talanta*, 1964, **11**, 1067.

Sulphosalicylic acid was employed as the indicator for the titration of iron at pH 2–3. Preliminary experiments revealed that the colour of the iron-sulphosalicylic acid complex is discharged only slowly after the addition of excess EDTA, when the amount of ammonium chloride added is not higher than that required to redissolve the bismuth oxychloride initially formed. But with the solution nearly saturated with ammonium chloride, the colour disappeares rapidly and with seemingly equivalent amounts of EDTA. However, the disappearance of the red colour at the end-point was only gradual, especially with a large excess of bismuth present. Thus, in this particular case, no visual end-point could be obtained and a photometric titration was used.

EXPERIMENTAL

Apparatus

The phototitrator described by Flaschka and Sawyer[5] was employed with a heat filter mounted in the light path.[6] An interference filter with the nominal wavelength of 508 mμ was used. All titrations were performed in a glass cell with a 2-cm path length and a 200-ml capacity.

Reagents

All solutions were prepared from reagent-grade materials. Deionised water was used exclusively.

An approximately 0·1*M EDTA solution* was prepared by dissolving 37 g of the disodium salt dihydrate and making the volume to 1 litre.

An approximately 0·1*M iron solution* was prepared by dissolving 40 g of iron(III) nitrate in 1 litre.

A 0·6*M bismuth solution* was prepared by dissolving 290 g of bismuth nitrate in water to which several ml of concentrated nitric acid had been added, and diluting to 1 litre.

The EDTA solution was standardised against 0·10000*M* zinc solution which had been prepared by dissolving 6·538 g of zinc metal (99·99% purity) in the minimum amount of dilute nitric acid, and diluting to 1 litre. The standardisation was performed by titration at pH 5, using Xylenol Orange as indicator. This EDTA solution was used as the reference in the standardisation of the iron(III) solution, using sulphosalicylic acid as indicator at pH 2–3 in a photometric titration. Appropriate dilutions of the stock solutions were performed in order to obtain 0·01*M* iron and EDTA solutions.

Ammonium chloride was used as the solid and as a saturated aqueous solution.

The *indicator solution* was prepared by dissolving 1 g of sulphosalicylic acid in 10 ml of water.

Procedure

An accurately measured amount of the metal ion solution was transferred to the titration cell and enough hot water was added to make the solution volume 75–100 ml. Then 20–30 g of solid ammonium chloride were added in 5-g portions, with vigorous stirring, until no more solid was observed to dissolve readily. The remaining solid was dissolved by adding small amounts of hot water, and the solution volume was then brought to about 150 ml with a saturated ammonium chloride solution. The solution was cooled to room temperature, and the pH was adjusted to between 2 and 3 by dropwise addition of dilute sodium hydroxide, with vigorous stirring to minimise the local precipitation of bismuth salts. The cell was positioned in the phototitrator, which was then adjusted to indicate a transmittance of 85–90%. Finally, 4–5 drops of indicator were added and the titration was carried out at 508 mμ in the usual manner, with 0·01–0·1*M* EDTA.

RESULTS AND DISCUSSION

The results of several titrations of iron(III), alone and in the presence of bismuth and other metals, are presented in Table I. Using the procedure presented above, solutions with a molar ratio of Bi:Fe of 2,100 were titrated, and showed the precision and accuracy to be expected with the apparatus and technique employed. When the ratio was increased to 3,000 and slightly above, a tendency towards increasing positive errors was observed. Impurities of iron or other titratable metals in the bismuth salt may be responsible for this trend, but it is more likely that at this high ratio some bismuth is also titrated.

TABLE I.—REPRESENTATIVE RESULTS FOR THE EDTA TITRATION OF IRON(III) IN THE PRESENCE OF BISMUTH AND SOME OTHER METAL IONS

Fe taken, *mg*	1·14 × $10^{-1}M$ EDTA, *ml*			Metal (M) added	Molar ratio M:Fe
	Calculated	Found	Difference		
5·70	0·89	0·89	0·00	—	—
5·70	0·89	0·88	−0·01	—	—
5·70	0·89	0·89	0·00	Bi	2
5·70	0·89	0·87	−0·02	Bi	2
5·70	0·89	0·88	−0·01	Bi	50
5·70	0·89	0·87	−0·02	Bi	100
5·70	0·89	0·89	0·00	Bi	210
5·70	0·89	0·90	+0·01	Bi	420
	5·70 × $10^{-2}M$ EDTA, *ml*				
2·85	0·89	0·90	+0·01	Bi	1050
	1·14 × $10^{-2}M$ EDTA, *ml*				
1·14	1·79	1·79	0·00	—	—
1·14	1·79	1·79	0·00	Bi	2100
1·14	1·79	1·80	+0·01	Bi	2090
1·14	1·79	1·87	+0·08	Bi	3140
1·14	1·79	1·86	+0·07	Bi	3140
	1·00 × $10^{-2}M$ EDTA, *ml*				
1·23	2·20	2·20	0·00	Bi	1570
1·14	2·05	2·08	+0·03	Bi	1450
1·14	2·05	2·14	+0·09	Al	9
1·14	2·05	2·47	+0·42	Al	9
1·14	2·05	2·04	−0·01	Zn	25
1·14	2·05	2·04	−0·01	Ca	25
1·14	2·05	2·04	−0·01	Pb	25
1·14	2·05	2·05	0·00	Pb	125
1·14	2·05	2·05	0·00	Co	50
1·14	2·05	2·04	−0·01	Co	250
1·14	2·05	2·06	+0·01	Hg(II)	500
1·14	2·05	2·06	+0·01	In	1
1·14	2·05	2·06	+0·01	In	10
1·14	2·05	2·05	0·00	Mn	125

The rate of fading of the colour of the iron-sulphosalicylic acid complex upon the addition of an increment of titrant solution decreases considerably for Bi:Fe ratios above 1,000, and it becomes necessary to wait 4–5 min for the reaction to go to virtual completion after each addition of titrant. However because only a few points are required for locating the end-point graphically, this delay is not too serious. A reasonable explanation for the delayed reaction may be suggested. As the EDTA is added to the solution containing such a high concentration of bismuth, complex formation first occurs with that metal; then the iron exchanges with the bismuth, and this exchange reaction takes place slowly.

A mole ratio, Bi:Fe, of 3,000 is equivalent to a weight ratio of approximately 11,200. Thus the situation in the artificial solutions parallels the determination of about 0·01% of Fe in a bismuth metal sample of which 12 g were taken. The determinations at this ratio were precise to about 4% relative. At these levels of amounts and ratios, the success of a titrimetric determination is rather unusual. It must, of course, be considered that in an actual analysis less favourable results may be obtained because of the presence of interfering impurities.

For the titration of iron at the high Bi:Fe ratios it is necessary to obtain the maximum amount of dissolved chloride. In order to incorporate as much ammonium chloride as possible, it is helpful to warm the saturated ammonium chloride solution in contact with excess solid salt, before using it to raise the volume of the solution in the titration cell to 150 ml.

Predictions about elements that may interfere with the iron titration may be made cautiously from a comparison of the stability constants, and from knowledge of the situation in the absence of extreme chloride concentrations. Because iron(III) is known to form chloro complexes, the effective stability constant of the iron(III)-EDTA complex may be lowered to such an extent that the metals which are of no influence under normal conditions may interfere at high chloride concentrations. Several metals were added in order to see if there was a noticeable effect on the position and quality of the end-point. No effects were observed with calcium, magnesium, mercury, indium, lead, manganese or zinc in solutions containing the ratios of metal:Fe indicated in Table I. No attempt was made to establish limiting ratios. Cobalt slowed the rate of reaction considerably at a ratio of 250. Nickel and copper could only be tolerated in concentrations up to about that of iron(III). As expected, aluminium interfered and high results were obtained, implying that this metal is partially titrated. Zirconium and hafnium were fully titrated under these conditions. Gallium, in contrast to indium, was not completely masked by the chloride and high results for iron were obtained at a ratio Ga:Fe as low as 1. Titanium slowed the reaction between iron and EDTA to such an extent that the titration became impracticable, even with equal concentrations of titanium and iron.

The interference studies reported are only exploratory in nature, because the main concern of the present investigation was masking of bismuth and the determination of iron. A study of the application of low stability masking with chloride, and of the exclusion of some interfering metals by addition of further masking agents is under way on a broader basis, and any results of interest will be published at a later date.

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Zusammenfassung—In Lösungen, die hohe Konzentrationen an Ammoniumchlorid enthalten, wird Wismut als Chlorokomplex maskiert; Eisen(III) kann dann mit AeDTE gegen Sulfosalicylsäure als Indicator photometrisch titriert werden. Bis zu einem Molverhältnis Bi/Fe von etwa 2000 werden gute Resultate erhalten. Bei höheren Verhältnissen ergeben sich leichte Überwerte. Der Einfluss einiger anderer Metall wird studiert.

Résumé—Dans les solutions à forte concentration en chlorure d'ammonium, le bismuth est dissimulé à l'état de chloro-complexe, et l'on peut doser le fer (III) au moyen d'EDTA, avec virage final photométrique, en utilisant comme indicateur l'acide sulfosalicylique. On obtient de bons résultats jusqu'à un rapport molaire Bi/Fe de 2000 environ. Pour des rapports plus grands, on obtient, pour le fer, des résultats légèrement trop élevés. On étudie l'influence de quelques autres ions métalliques sur le dosage.

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SOME ANTIPYRINE DERIVATIVES IN THE ANALYTICAL CHEMISTRY OF THE PLATINUM METALS

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Summary—The reaction of quadrivalent osmium and iridium with antipyrine and some of its derivatives has been studied, and it has been shown that in acidic solutions the compounds $(R.H)_2MeX_6$ are formed. The extraction of the halide complexes of osmium, iridium, ruthenium, rhodium, platinum and palladium with diantipyrylpropylmethane by dichloroethane has been investigated. An extraction–photometric method is proposed for determining 2–20 μg/ml of osmium in the presence of 40 mg of ruthenium and for determining 4–40 μg/ml of iridium in the presence of 4 mg of rhodium. The error of the determination is $\pm 10\%$. A gravimetric method is proposed for determining 5–13 mg of osmium and iridium with diantipyrylpropylmethane and diantipyrylmethane. The error of the determination is $\pm 3\%$. The possibility is shown of the extractive separation of small amounts of iridium and rhodium, platinum and rhodium, and palladium and rhodium, using diantipyrylpropylmethane.

The platinum metals form stable complex anions with a number of monodentate inorganic ligands. During the analysis of the platinum metals, they frequently pass into solution in the form of anionic chloride and bromide complexes: $Me^{IV}X_6^{2-}$ and $Me^{II}X_4^{2-}$. where X is Cl^- or Br^- and Me is a platinum metal. These anions form compounds with many organic bases. Some of the organic bases (strychnine,[1–3] brucine,[4] acridine,[5,6] tetraphenylarsonium chloride,[7–10] fatty amines[15]), and tributyl phosphate,[11–14] have been used for the gravimetric and photometric determination or extractive separation of the platinum metals.

We have made a detailed study of the reaction of the halide complexes of the platinum metals with antipyrine and its derivatives (diantipyrylmethane, diantipyrylpropylmethane and diantipyrylphenylmethane) in order to develop new and improved analytical methods for the determination and separation of the platinum metals. These reagents are widely used in analytical chemistry at the present time. In acid solutions they are present in the form of cations, and these react with the anionic metal complexes:

$$[Me^mX_n]^{-(m-n)} + (m + n)RH^+ \rightleftharpoons (RH)_{(m-n)}[Me^mX_n] \qquad (1)$$

It was found that quadrivalent osmium, iridium and platinum, and also bivalent platinum and palladium, are precipitated from hydrochloric acid solutions (0·5–2M) and hydrobromic acid solutions by antipyrine, diantipyrylmethane, diantipyrylpropylmethane and diantipyrylphenylmethane. The compounds formed possess valuable analytical properties—a high molecular weight, low water solubility, the capacity for being extracted with organic solvents, a characteristic coloration, *etc.* We have used these properties to develop extraction-photometric and gravimetric methods for the determination of osmium and iridium and for the extractive separation of rhodium from platinum, palladium and iridium.

EXPERIMENTAL

Reagents

Osmium, ruthenium, iridium and platinum were used in the form of the following salts: $(NH_4)_2OsCl_6$, $(NH_4)_2OsBr_6$;[16] $(NH_4)_2RuOHCl_5$;[17] $(NH_4)_2RuOHBr_5$;[18] $(NH_4)_2IrCl_6$;[19] $(NH_4)_2IrBr_6$;[20] $(NH_4)_2PtCl_6$;[21] $(NH_4)_2PtBr_6$.[22]

The content of metal in the products was determined by calcining a weighed sample in a current of hydrogen (in air in the case of the platinum preparation) to constant weight of metallic osmium, ruthenium, iridium or platinum. Standard solutions were prepared by dissolving weighed amounts of the salts.

The hydrochloric and hydrobromic acid solutions of the rhodium and palladium salts were prepared from metallic rhodium and palladium by known methods.[23–25] The contents of rhodium and palladium in the prepared solutions were determined gravimetrically by means of thionalide[26] and dimethylglyoxime,[27] respectively.

The antipyrine was a commercial preparation with a melting point of 113·5–114·5°. The diantipyrylmethane,[28] diantipyrylpropylmethane[29] and diantipyrylphenylmethane[30] were synthesised from antipyrine by condensing it with the corresponding aldehydes. The materials obtained were purified by recrystallisation from ethanol.

Preparation and Composition of Compounds of Osmium(IV) and Iridium(IV) with Antipyrine and Its Derivatives

When acidic solutions of $(NH_4)_2OsCl_6$, $(NH_4)_2OsBr_6$, $(NH_4)_2IrCl_6$ or $(NH_4)_2IrBr_6$ and of the various antipyrine derivatives were mixed, curdy precipitates of low water-solubility immediately separated. To study the composition and properties of these precipitates, they were obtained in a pure state by the following method.

A hydrochloric (or hydrobromic) acid solution, containing 20–30 mg of osmium or iridium in the form of $(NH_4)_2OsCl_6$, $(NH_4)_2OsBr_6$, $(NH_4)_2IrCl_6$ or $(NH_4)_2IrBr_6$, was treated with 5–8 ml of a 2% solution of diantipyrylmethane, diantipyrylpropylmethane or diantipyrylphenylmethane in acetic acid (1:1).* The curdy precipitates which separated were filtered off and washed three or four times with water acidified with hydrochloric acid (or hydrobromic acid) and then three or four times with water alone.

The materials obtained were purified by recrystallisation from a 1:1 mixture of methanol and acetone and were analysed for their contents of osmium and iridium by calcining a weighed sample in a current of hydrogen to constant weight of metallic osmium or iridium.

Table I gives the formulae of the compounds (from the results of chemical analysis) and also some of their properties.

To elucidate the structure of the compounds, their infrared spectra were recorded in the crystalline state. The spectra were taken on a IKS-14 spectrophotometer in Nujol over the frequency range 4000—700 cm^{-1}.

As can be seen from Table II (Fig. 1), the band of carbonyl absorption at 1650–1660 cm^{-1}, present in antipyrine, diantipyrylmethane and diantipyrylpropylmethane,

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* Because of their high solubility in water, the compounds with antipyrine were isolated by adding dry antipyrine to a solution of the osmium or iridium salt.

TABLE I.—COMPOSITION AND PROPERTIES OF THE COMPOUNDS OF OSMIUM (IV) AND IRIDIUM (IV) WITH ANTIPYRINE AND ITS DERIVATIVES OBTAINED

Formula[a]	Colour and form of crystals	λ_{max}, *mμ*	ε	Solubility in 0·5*M* HCl, *moles/l.*
$(C_{11}H_{12}ON_2{\cdot}H)_2OsCl_6$	Yellow			Very soluble
$(C_{23}H_{24}O_2N_4{\cdot}H)_2OsCl_6$		346	10600	$10{\cdot}7 \times 10^{-5}$
$(C_{26}H_{30}O_2N_4{\cdot}H)_2OsCl_6$		378	8000	$3{\cdot}5 \times 10^{-5}$
$(C_{29}H_{28}O_2N_4{\cdot}H)_2OsCl_6$				$1{\cdot}8 \times 10^{-5}$
$(C_{11}H_{12}ON_2{\cdot}H)_2OsBr_6$	Dark red	425	6000	Very soluble
$(C_{23}H_{24}O_2N_4{\cdot}H)_2OsBr_6$		457	9500	$3{\cdot}7 \times 10^{-5}$
$(C_{26}H_{30}O_2N_4{\cdot}H)_2OsBr_6$		500	6500	—
$(C_{29}H_{28}O_2N_4{\cdot}H)_2OsBr_6$				—
$(C_{11}H_{12}ON_2{\cdot}H)_2IrCl_6$	Dark red			Very soluble
$(C_{23}H_{24}O_2N_4{\cdot}H)_2IrCl_6$		442	4500	$14{\cdot}2 \times 10^{-5}$
$(C_{26}H_{30}O_2N_4{\cdot}H)_2IrCl_6$		498	5000	$3{\cdot}8 \times 10^{-5}$
$(C_{23}H_{28}O_2N_4{\cdot}H)_2IrCl_6$				$1{\cdot}1 \times 10^{-5}$
$(C_{11}H_{12}ON_2{\cdot}H)_2IrBr_6$	Dark blue needles or plates	540	2300	—
$(C_{23}H_{24}O_2N_4{\cdot}H)_2IrBr_6$		555	2300	—
$(C_{26}H_{30}O_2N_4{\cdot}H)_2IrBr_6$		605	4150	—
$(C_{29}H_{28}O_2N_4{\cdot}H)_2IrBr_6$		700	2150	—

[a] $C_{11}H_{12}ON_2$—antipyrine; $C_{23}H_{24}O_2N_4$—diantipyrylmethane; $C_{26}H_{30}O_2N_4$—diantipyrylpropylmethane; $C_{29}H_{28}O_2N_4$—diantipyrylphenylmethane.

TABLE II.—FREQUENCIES OF THE VIBRATIONS OF SOME GROUPS OF ANTIPYRINE, ITS DERIVATIVES AND THEIR SALTS

Compound	Frequency of bond, *cm*$^{-1}$			
	C═O	C═C	HO—	C$\overset{...}{=}$O · · · HX
$C_{11}H_{12}ON_2$	1662	1586	—	—
$(C_{11}H_{12}ON_2{\cdot}H)_2OsBr_6$	—	2573	3560m	2452s
		1593	3470s	
			3226s	1830m
$(C_{11}H_{12}ON_2{\cdot}H)_2OsCl_6$	—	1576	3470m	—
			3070s	
		1616	—	—
$(C_{23}H_{24}O_2N_4$	1656	1592	—	—
		1620	3058s	2205s
$C_{23}H_{24}O_2N_4{\cdot}HCl$	—	1590		
		1605	3370w	2240w
$(C_{23}H_{24}O_2N_4{\cdot}H)_2OsBr_6$	—	1584	3000w	
$(C_{23}H_{24}O_2N_4{\cdot}H)_2OsCl_6$	—	1597	3450w	—
		1596	3470s	2470w
$(C_{23}H_{24}O_2N_4{\cdot}H)_2IrBr_6$	—	1588	3280w	
$C_{26}H_{30}O_2N_4$	1658; 1650	1595	—	—
$(C_{26}H_{30}O_2N_4{\cdot}H)_2OsBr_6$	—	1610	3400w	2400w
		1598	3480w	—
$(C_{26}H_{30}O_2N_4{\cdot}H)_2OsCl_6$	—	1584		
$(C_{26}H_{30}O_2N_4{\cdot}H)_2IrBr_6$	—	1596	3470w	2400w
		1582		

m = medium-intensity, s = strong, w = weak.

disappears and bands of comparatively low intensity appear in the region of 1500–1560 cm^{-1}. In the region of absorption of the O—H and $\overset{+}{\mathrm{N}}$—H groups, broad intense bands appear (3500–3000 cm^{-1}), the intensity of these bands in the antipyrine complexes being considerably higher than in the diantipyrylmethane and diantipyrylpropylmethane complexes. A number of the spectra are characterised by intense absorption in the region of 3500–1800 cm^{-1}.

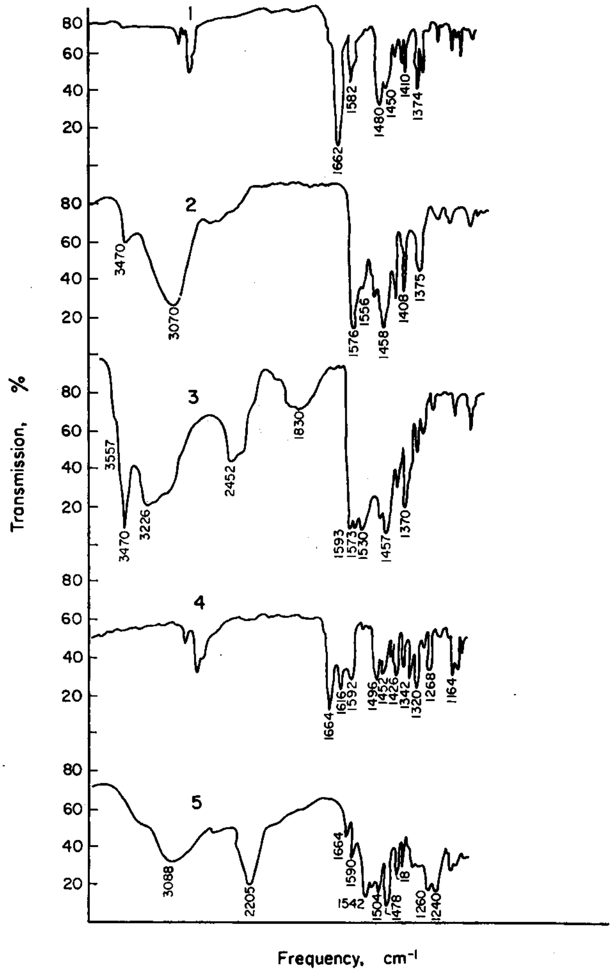
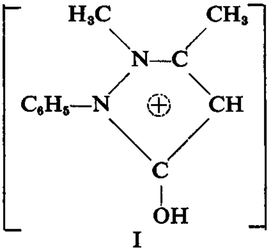


FIG. 1.—Infrared spectra of compounds in the crystalline state (in Nujol):

1. antipyrine,
2. antipyrine hexachloro-osmate,
3. antipyrine hexabromo-osmate,
4. diantipyrylmethane,
5. diantipyrylmethane hydrochloride.

The assignment of the absorption bands, in the complexes investigated, in the region of 3500—3000 cm^{-1} to the stretching vibrations of the $\overset{+}{\mathrm{N}}$—H bond does not agree with the behaviour of the carbonyl band. In fact, the interaction of the protons with the N_1 or N_2 nitrogen atoms must lead to a displacement of the C=O band to the high-frequency region, *i.e.*, under these conditions, the conjugation of the C=O bond with the unshared pair of electrons of the nitrogen atom will decrease and their electronegativity will increase.[31]

Thus, the appearance of bands in the region of 3500–3000 cm^{-1} in compounds of antipyrine and its derivatives with acids is connected with the addition of a proton to the carbonyl oxygen atom with subsequent opening of the carbonyl bond and formation of a hydroxyl group, which leads to the formation of onium salts of types I and Ia.



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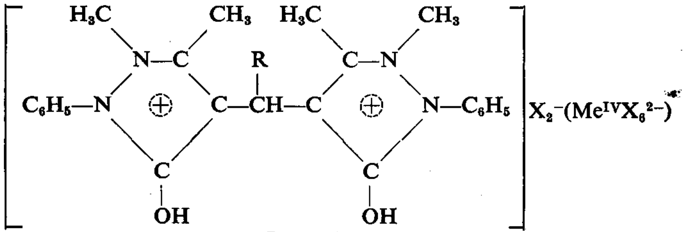


Ia

However, the appearance in the spectra of the compounds studied (Fig. 1, Table II) of absorption bands in the region of 2500–1800 cm^{-1} evidently shows an interaction of the antipyrine cation with the anions not only through electrostatic forces but also as a consequence of the formation of hydrogen bonds:

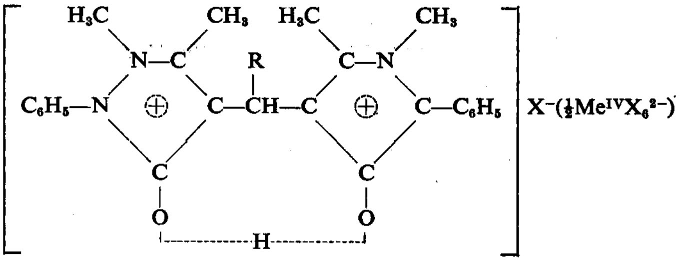
$$>\mathrm{C—O—H}\cdots\mathrm{X}\,(\mathrm{H_2MeX_6}) \rightleftharpoons >\mathrm{C}\overset{\cdots}{=}\mathrm{O}\cdots\mathrm{HX}\,(\mathrm{H_2MeX_6}).$$

The bands in the region of 1500–1560 cm^{-1} are apparently connected with the absorption of the strongly polarised $\mathrm{C}\overset{\cdots}{=}\mathrm{O}$ bond in the complexes

$$>\mathrm{C}\overset{\cdots}{=}\mathrm{O}\cdots\mathrm{HX}\,(\mathrm{H_2MeX_6}).$$

The considerably increased intensity of the hydroxyl absorption bands in the compounds of diantipyrylmethane and diantipyrylpropylmethane with osmium(IV) and iridium(IV) is probably connected with the formation of strong intramolecular hydrogen bonds between one proton and two carbonyl oxygen atoms (see formula II below). This is in agreement with the aromatic nature of antipyrine. In actual fact, in the formation of complex II (see below), the proton evidently adds first to one of the two carbonyl oxygen atoms in the diantipyrylmethane (or diantipyrylpropylmethane) with subsequent formation of a strong intramolecular hydrogen bond in which the proton is attached to the two carbonyl oxygen atoms to the same extent. The intensity of the absorption of such hydroxyl groups is particularly strongly reduced.[32]

The results obtained on the structure of the compounds of antipyrine and its derivatives with quadrivalent osmium and iridium are in good agreement with the fact that in all of the compounds formed in an acidic medium antipyrine and its



II

derivatives participate as singly charged cations (see I above). This fact is difficult to explain if the basicity of antipyrine and its derivatives is connected with the basicity of the heterocyclic nitrogen atoms. In actual fact, in the case of antipyrine, the formation of a singly charged cation can be connected formally with a weakening of the basic properties of the nitrogen present in the α-position to the C=O group. In the case of diantipyrylmethane, diantipyrylpropylmethane and other derivatives having two nitrogen atoms of equivalent basicity in the molecule, however, it is difficult to see why protonation takes place only in respect of one of them.

Thus, the compounds of antipyrine and its derivatives that have been obtained with quadrivalent osmium and iridium are, in the crystalline state, salts of the cations of antipyrine, diantipyrylmethane and diantipyrylpropylmethane with the anions $OsCl_6^{2-}$, $OsBr_6^{2-}$, $IrCl_6^{2-}$ and $IrBr_6^{2-}$. The formation of these compounds may be expressed by the equation:

$$2R + Me^{IV}X_6^{2-} + 2H^+ \leftrightharpoons (R{\cdot}H)_2MeX_6.$$

Solubility of Compounds of Osmium(IV) and Iridium(IV) with Antipyrine and Its Derivatives in Aqueous Solution

The hexachloro- and hexabromo-osmates and the hexachloro- and hexabromo-iridates of diantipyrylmethane, diantipyrylpropylmethane and diantipyrylphenylmethane are sparingly soluble in water, but readily soluble in certain organic solvents—dichloroethane and chloroform. The compounds of osmium(IV) and iridium(IV) with antipyrine, on the other hand, are readily soluble in water and sparingly soluble in organic solvents. As a rule, the bromine-containing complexes are less soluble in water than the corresponding chlorine-containing complexes (see Table I).

The influence of the concentrations of the acid, the reagent and alkali-metal chlorides on the solubility of diantipyrylpropylmethane hexachloro-osmate and -iridate and of diantipyrylmethane hexabromo-osmate has been studied. The procedure used was as follows.

A freshly produced precipitate, carefully washed with water, was placed in a bottle containing 50 ml of hydrochloric acid (or hydrobromic acid) of the appropriate concentration and shaken in a thermostat at 25° for 2–3 hr (it was established by preliminary experiments that this time was sufficient for saturation). The resulting saturated solution was rapidly filtered through filter paper, the first portion of the filtrate being rejected. The content of metal in an aliquot of the clear filtrate was determined: osmium with thiourea[33] or with diantipyrylpropylmethane (for the method, see below), and iridium with diantipyrylpropylmethane (for the method, see below).

The results obtained are given in Figs. 2–4. In the presence of sodium chloride, the solubility of the iridium compound diminishes somewhat; the solubility of the osmium compound remains practically unchanged.

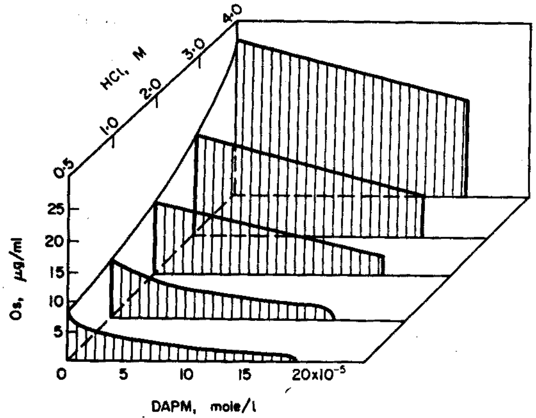


FIG. 2.—Influence on the solubility of $(C_{26}H_{30}O_2N_4{\cdot}H)_2OsCl_6$ of the concentration of hydrochloric acid and diantipyrylpropylmethane (DAPM).

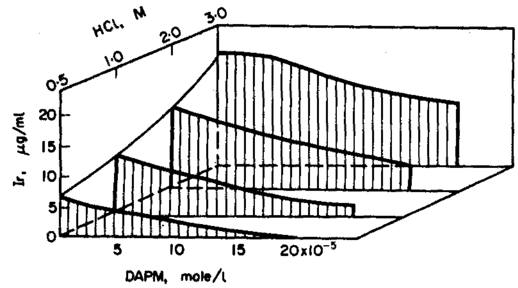


FIG. 3.—Influence on the solubility of $(C_{26}H_{30}O_2N_4{\cdot}H)_2IrCl_6$ of the concentration of hydrochloric acid and diantipyrylpropylmethane (DAPM).

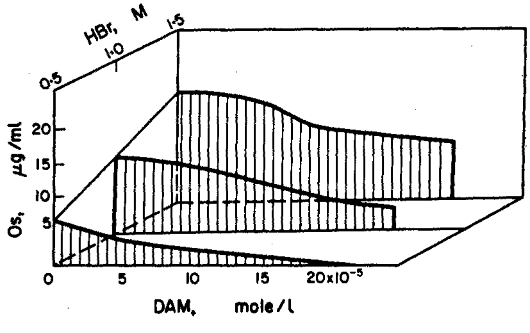


FIG. 4.—Influence on the solubility of $(C_{23}H_{24}O_2N_4{\cdot}H)_2OsBr_6$ of the concentration of hydrobromic acid and diantipyrylmethane (DAN).

Extractability of Osmium and Iridium, and also of Platinum, Palladium, Ruthenium and Rhodium with Dichloroethane in Presence of Diantipyrylpropylmethane

In the presence of diantipyrylpropylmethane, quadrivalent osmium, iridium, platinum and ruthenium, and also bivalent palladium, are well extracted by dichloroethane from hydrochloric and hydrobromic acid solutions.

Tervalent ruthenium, rhodium and iridium are extracted considerably less well.

TABLE III.—EXTRACTABILITY OF CHLORIDES OF COMPLEXES OF PLATINUM, PALLADIUM, IRIDIUM AND RHODIUM FROM HYDROCHLORIC ACID SOLUTIONS (1*M*) WITH DICHLOROETHANE IN PRESENCE OF DIANTIPYRYLPROPYLMETHANE[a]

Metal	Metal taken, *mg*	Metal found, *mg*		Percentage extraction, E	Distribution coefficient, D[b]
		Aqueous phase	Organic phase		
Pt^{IV}	5·28	0·01	5·30	99·8	—
	6·60	0·01	6·60	99·8	—
	7·92	0·01	8·00	99·8	—
Pd^{II}	3·12	0·02	3·11	99·2	—
	6·24	0·05	6·15	99·2	—
	4·68	0·03	4·70	99·4	—
Ir^{IV}	1·31	0·02	1·29	98·5	129
	5·24	0·08	5·15	98·5	132
	7·86	0·12	7·85	98·6	125
Rh^{III}	5·11	0·45	0·78	15·3	0·35
	10·23	8·80	2·50	14·7	0·34
	10·23	8·80	1·54	15·0	0·35

[a] Extraction carried out with 10 ml of a 1% solution of diantipyrylpropylmethane in dichloroethane. Contents of platinum, palladium, iridium and rhodium in each of the phases determined by means of tin(II) chloride.[34–37]

[b] $$D = \frac{\text{mg/ml of metal in organic phase}}{\text{mg/ml of metal in aqueous phase}}.$$

The greatest difference in extractability is found with hydrochloric acid solutions. Thus, the extractability of osmium is 94–96%, of iridium 98·5%, of platinum > 99%, of palladium > 99%, of ruthenium(IV) 96·5%, of ruthenium(III) 1·5% and of rhodium(III) 15%, in extraction from solutions 1*M* with respect to hydrochloric acid by a 1% solution of the reagent in dichloroethane (Tables III and IV).

The extractability of the platinum metals depends on the acidity of the aqueous solution and on the excess of reagent.

A 6- to 10-fold excess of diantipyrylpropylmethane is sufficient for the complete extraction of osmium(IV), iridium(IV), platinum(IV) and palladium(II) (Fig. 5; the study was carried out spectrophotometrically from the optical density of the extracts).

TABLE IV.—EXTRACTABILITY OF CHLORIDES OF COMPLEXES OF RUTHENIUM AND OSMIUM FROM HYDROCHLORIC ACID SOLUTIONS (1*M*) WITH DICHLOROETHANE IN PRESENCE OF DIANTIPYRYLPROPYLMETHANE[a]

Concentration of reagent solution, %	Percentage extraction, E		
	Ru^{IV} (64 μg/ml)	Ru^{III} (3·15 mg/ml)	Os^{IV} (8 μg/ml)
0·1	33·8	0·4	96·28
0·2	41·0	0·6	94·9
1·0	80·6	1·3	—
2·0	93·5	2·8	—
3·0	95·0	3·6	—
4·0	96·5	5·6	—

[a] Extraction carried out with 10 ml of a solution of the given concentration of the reagent in dichloroethane (volume of aqueous phase: 20 ml). Extraction of osmium and ruthenium studied by means of the radioactive isotopes ^{191}Os and $^{106}Ru + {}^{106}Rh$.

Ruthenium(IV) requires a 150-fold excess of the reagent (Table IV). The percentage extraction of tervalent ruthenium and of rhodium, even with a large excess of diantipyrylpropylmethane, did not exceed 6% and 15%, respectively (Tables IV and V).

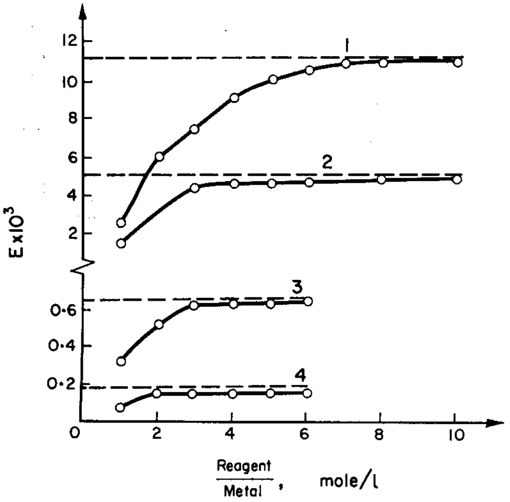


FIG. 5.—Influence of an excess of diantipyrylpropylmethane on the extraction of:
1. osmium, 3. platinum,
2. iridium, 4. palladium.

The extractability of osmium(IV), iridium(IV), platinum(IV) and palladium(II) remains practically constant over a wide range of concentrations of acid (0.5–5M hydrochloric acid) (Fig. 6). The percentage extraction of ruthenium and rhodium (Table VI) decreases with an increase in the concentration of the hydrochloric acid.

Photometric Method for Determination of Osmium(IV) and Iridium(IV) by Means of Antipyrine Derivatives

The dichloroethane extracts of quadrivalent osmium and iridium are intensely coloured. The absorption curves (Fig. 7) for all three complexes of osmium and

TABLE V.—EXTRACTABILITY OF RHODIUM FROM HYDROCHLORIC ACID SOLUTIONS (1M) IN PRESENCE OF DIANTIPYRYLPROPYLMETHANE[a]

Concentration of reagent solution, %	Rh taken, *mg*	Rh found in organic phase, *mg*	Percentage extraction, E
0·1	24·70	0·60	2·4
0·2	0·99	0·66	6·0
0·2	1·97	0·09	4·5
0·2	2·96	0·13	4·4
0·2	3·95	0·18	4·5
0·5	24·70	1·30	5·3
1·0	10·23	1·55	15·15

[a] Extraction carried out with 10 ml of a solution of the given concentration of the reagent in dichloroethane (volume of aqueous phase: 20 ml).

TABLE VI.—DEPENDENCE OF EXTRACTION OF RHODIUM ON ACIDITY OF INITIAL SOLUTION[a]

HCl, *M*	Rh found in organic phase, *mg*	Percentage extraction, E
0·5	0·74	3·0
1·0	0·66	2·7
2·0	0·49	2·0
3·0	0·46	1·9
4·0	0·44	1·8
5·0	0·42	1·7
6·0	0·40	1·6
7·0	0·10	0·4
8·0	none	0·0

[a] 24·70 mg of Rh taken.

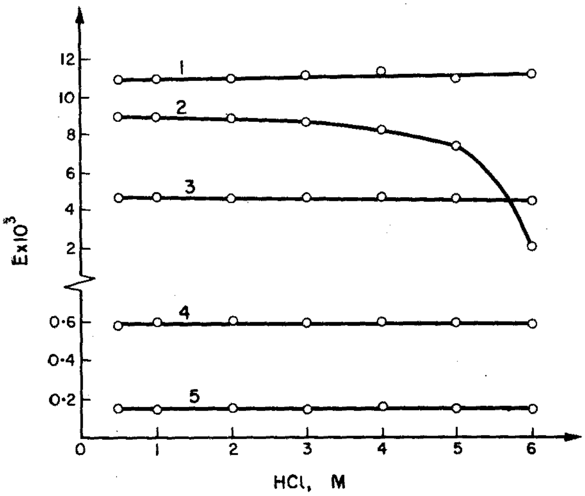


FIG. 6.—Influence of the concentration of hydrochloric acid on the extraction of:

1. osmium,
2. ruthenium(IV)
3. iridium,
4. platinum,
5. palladium.

iridium with diantipyrylmethane, diantipyrylpropylmethane and diantipyrylphenylmethane are identical with one another, and the coefficients of molar absorption are practically the same. Curves 2 and 4 (Fig. 7) show the light absorption of solutions of ammonium hexachloro-osmate and -iridate in 1*M* hydrochloric acid, respectively. By comparing curves 1 and 2 with 3 and 4, the light absorption of the extracts arises from the absorption of the $OsCl_6^{2-}$ and $IrCl_6^{2-}$ anions. A slight displacement of the absorption curves of the extracts to the long-wave region of the spectrum and an increase in the intensity of the absorption are connected with the replacement of the ammonium cation in the compounds $(NH_4)_2MeX_6$ by the large organic cations $(C_{23}H_{24}O_2N_4{\cdot}H)^+$, $(C_{26}H_{30}O_2N_4{\cdot}H)^+$ and $(C_{29}H_{28}O_2N_4{\cdot}H)^+$ and with the change of solvent. Analogous phenomena are found in the case of the bromine-containing compounds. The light-absorption curves of solutions of the pure materials in dichloroethane proved to be identical with the absorption curves of the extracts.

It was found by the method of isomolar series that the ratio of metal to reagent in the extracted compounds was 1:2, *i.e.*, the extracted compounds had the same composition as those isolated in the crystalline state.

The optical density of the extracts is proportional to the concentration in the range 2–20 μg/ml of osmium and 4–40 μg/ml of iridium. This has permitted the development of simple photometric methods for determining osmium and iridium.

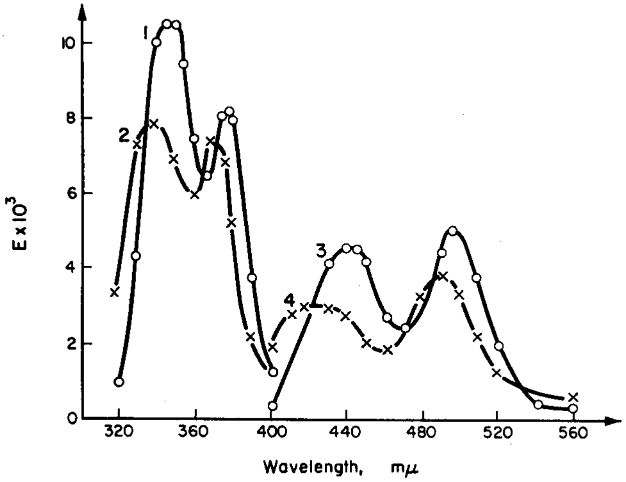


FIG. 7.—Absorption curves of the chlorides of complexes of osmium (1) and iridium (3) with antipyrine derivatives, and of ammonium hexachloro-osmate (2) and ammonium hexachloro-iridate (4).

The most suitable reagent for the extraction and subsequent photometric determination of osmium and iridium is diantipyrylpropylmethane and the most suitable organic solvent is dichloroethane.

Ruthenium does not interfere with the determination of osmium if it is first converted to the tervalent state. As mentioned above, in the presence of a small excess of reagent (10 ml of a 0·1% solution in dichloroethane for 0·8 mg of osmium) it is not appreciably extracted.

Rhodium does not interfere with the determination of iridium if the content of the former in the initial solution does not exceed 4 mg. In this case, the amount of rhodium passing into the organic phase does not exceed 0·2 mg (on extraction with a 0·2% solution of the reagent). The light absorption of an extract containing 0·2 mg of rhodium at 498 mμ (maximum of the light absorption of the iridium complex) is insignificant.

After a detailed study of the reaction of osmium and iridium tetrachlorides with the antipyrine derivatives and an investigation of the behaviour of the other platinum metals under the conditions of the formation of the osmium and iridium complexes, extraction-photometric methods were developed for the determination of osmium in the presence of ruthenium and of iridium in the presence of rhodium. The methods are simple to carry out and are as follows.

Determination of osmium in presence of ruthenium. A hydrochloric acid solution (3–6*M* with respect to this acid), containing osmium in the form of $OsCl_6^{2-}$ and ruthenium, is heated with hydrazine hydrochloride or hydrazine sulphate for 10–15 min until the dark red colour of the solution changes to pale yellow. Under these conditions, the ruthenium is reduced to the tervalent state while the osmium remains in the quadrivalent state.

After cooling, the solution is transferred to a separating funnel and the osmium tetrachloride extracted with 10 ml of a 0·1 % solution of diantipyrylpropylmethane in dichloroethane. The optical density of the extract is measured at 346 mµ or 378 mµ and the osmium content found from a calibration curve. The method permits the determination of 2–20 µg of osmium/ml in the presence of 40 mg of ruthenium (Table VII).

TABLE VII.—SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM AND IRIDIUM WITH DIANTIPYRYLPROPYLMETHANE

Amount taken, µg		Amount added, mg		Found, µg		Error, %	
Os	Ir	Ru	Rh	Os	Ir	Os	Ir
19·0	—	6·10	—	19·0	—	0·0	—
38·0	—	30·52	—	39·7	—	+4·5	—
57·0	—	27·46	—	62·5	—	+9·6	—
171·2	—	18·30	—	163·0	—	−4·8	—
152·1	—	36·61	—	150·0	—	−1·3	—
133·1	—	45·76	—	141·0	—	+5·9	—
114·1	—	18·30	—	110·0	—	−3·6	—
—	38·6	—	0·988	—	40·5	—	+4·9
—	77·2	—	4·09	—	75·3	—	−2·5
—	347·6	—	4·09	—	351·4	—	+1·1
—	38·6	—	2·04	—	36·7	—	−4·9
—	154·5	—	3·952	—	152·5	—	−1·2
—	77·2	—	1·976	—	81·1	—	+5·0
—	231·7	—	1·02	—	237·5	—	+2·5

The error of the above determination is ±10%. Thus, the extraction-photometric method for determining osmium by means of diantipyrylpropylmethane is not inferior in sensitivity to the widely used thiourea method,[33] but its selectivity is superior to that of all known photometric methods of determining osmium.

The method may be used for the analysis of hydrochloric acid distillates and other solutions of osmium after this had been converted to $OsCl_6^{2-}$.

Determination of iridium in presence of rhodium. A solution, containing iridium and not more than 4 mg of rhodium, is twice evaporated on a water-bath with concentrated hydrochloric acid, in the presence of sodium chloride and hydrogen peroxide, to the state of moist salts to convert the iridium to $IrCl_6^{2-}$. The residue is dissolved in water, the solution transferred to a separating funnel and the iridium extracted with 10 ml of a 0·2 % solution of diantipyrylpropylmethane in dichloroethane. The optical density of the extract is measured at 490 mµ and the content of iridium found from a calibration curve. The method permits the determination of 4–40 µg of iridium/ml in the presence of up to 4 mg of rhodium with an accuracy of ±10 % (Table VII).

The extraction-photometric method for determining iridium by means of diantipyrylpropylmethane is equal in sensitivity to the method used in practice,[38–40] being inferior in this respect to the majority of other photometric methods for determining iridium. However, it is favourably distinguished from them in respect of selectivity, permitting the determination of up to 4 µg/ml in the presence of 100-fold amounts of rhodium. In our opinion, the method can be used for the analysis of any solution of iridium after its conversion to $IrCl_6^{2-}$.

The extraction-photometric determination of osmium and iridium in the form of the bromide complexes is not selective, *i.e.*, all platinum metals, including tervalent ruthenium and rhodium, are extracted well from hydrobromic acid solutions with the formation of coloured extracts.

Gravimetric Methods for Determination of Osmium and Iridium by means of Antipyrine Derivatives

Because the development of gravimetric methods for osmium and iridium is of practical importance, we have studied the possibility of using for this purpose the compounds of quadrivalent osmium and iridium with antipyrine derivatives that we have obtained.

Diantipyrylmethane (with precipitation from hydrobromic acid solution) and diantipyrylpropylmethane (with precipitation from hydrochloric acid solution) must be considered the most suitable reagents for the gravimetric determination of osmium and iridium. Diantipyrylphenylmethane is unsuitable because of the low solubility of its hydrochloride and hydrobromide. For the same reason, it is also undesirable to use diantipyrylpropylmethane in precipitation from hydrobromic acid solutions.

In the presence of a small excess of the reagent, quadrivalent osmium and iridium are precipitated practically completely from hydrochloric acid solutions by diantipyrylpropylmethane; quadrivalent osmium is also precipitated quantitatively from hydrobromic acid solutions by diantipyrylmethane (Figs. 2–4). Thus, in a solution $0{\cdot}5M$ with respect to hydrochloric acid and containing 20×10^{-5} mole/l. of reagent in excess, osmium cannot be detected with thiourea[33] nor iridium with a mixture of acids (H_2SO_4—H_3PO_4—$HClO_4$). From the results obtained, a gravimetric method for the determination of osmium and iridium has been developed.

Determination of osmium and iridium. A 2% solution of diantipyrylpropylmethane (or diantipyrylmethane in precipitation from hydrobromic acid solutions) in acetic acid (1:1) is added slowly with stirring to 60–70 ml of hydrochloric acid solution ($0{\cdot}1$–$0{\cdot}5M$) or a corresponding hydrobromic acid solution, containing osmium in the form of $OsCl_6^{2-}$ or $OsBr_6^{2-}$ or iridium in the form of $IrCl_6^{2-}$, until the addition of a fresh portion of the reagent causes no further precipitation. A further 1 ml of the reagent solution is then added and the solution containing the precipitate is allowed to stand for 2–3 hr. The resulting precipitate is filtered off through a No. 4 filter crucible, washed 4–5 times with a 0·05–0·1% solution of the reagent in $0{\cdot}5M$ hydrochloric acid, dried to constant weight at 100–110° and weighed. As can be seen from Table VIII, using diantipyrylmethane and diantipyrylpropylmethane it is possible to determine 5–13 mg of osmium and iridium by precipitation and weighing in the form of $(C_{26}H_{30}O_2N_4{\cdot}H)_2OsCl_6$, $(C_{23}H_{24}O_2N_4{\cdot}H)_2OsBr_6$ or $(C_{26}H_{30}O_2N_4{\cdot}H)_2IrCl_6$.

The error of the above determination is ±3%. Platinum and palladium interfere with the determination, forming sparingly soluble compounds with the antipyrine derivatives. Ruthenium and rhodium, although they do not give sparingly soluble compounds, nevertheless undergo considerable coprecipitation with the osmium and iridium precipitates. Thus, they precipitate to the extent of 2–3% from hydrochloric acid solutions of quadrivalent and tervalent ruthenium, as was found by means of the $^{106}Ru + {}^{106}Rh$ isotope. On precipitation from hydrobromic acid solutions, the amount of quadrivalent ruthenium coprecipitated increases to 20% and that of tervalent ruthenium to 7%.

The gravimetric methods for the determination of osmium and iridium by means of diantipyrylmethane and diantipyrylpropylmethane are favourably distinguished from many other gravimetric methods, firstly, because they do not require calcination of the precipitate to the metal and, secondly, because they permit the determination of milligram-amounts of osmium and iridium with great accuracy because of the small conversion factor to the metal. The disadvantage of these methods is their low selectivity: all platinum metals interfere with the determination.

TABLE VIII.—GRAVIMETRIC DETERMINATION OF OSMIUM AND IRIDIUM BY MEANS OF ANTIPYRINE DERIVATIVES

Form of precipitate	Amount taken, *mg*		Found, *mg*		Error, %	
	Os	Ir	Os	Ir	Os	Ir
	6·06	—	6·15	—	+1·5	—
$(C_{26}H_{30}O_2N_4{\cdot}H)_2OsCl_6$	8·65	—	8·55	—	−1·1	—
	4·33	—	4·47	—	+3·2	—
Factor = 0·1503	10·38	—	10·16	—	−2·1	—
	12·98	—	12·75	—	−1·8	—
	4·11	—	4·20	—	+2·2	—
$(C_{23}H_{24}O_2N_4{\cdot}H)_2OsBr_6$	3·69	—	3·69	—	0·0	—
	5·75	—	5·66	—	−1·5	—
Factor = 0·1314	8·21	—	8·03	—	−2·2	—
	7·80	—	7·88	—	+1·0	—
	—	5·24	—	5·19	—	−0·9
$(C_{26}H_{30}O_2N_4{\cdot}H)_2IrCl_6$	—	10·48	—	10·14	—	−3·2
	—	13·10	—	13·13	—	+0·2
Factor = 0·1523	—	8·52	—	8·68	—	+1·9
	—	6·55	—	6·55	—	0·0

Extractive Separation of Iridium and Rhodium, Platinum and Rhodium, and Palladium and Rhodium by means of Diantipyrylpropylmethane

The difference in extractability of iridium(IV), platinum(IV), palladium(II) and rhodium(III) has permitted the development of an extraction method for separating small amounts (6–10 mg) of rhodium and iridium, rhodium and platinum, and rhodium and palladium with the aid of diantipyrylpropylmethane.

Before separation, the solution containing the platinum metals was evaporated three times with concentrated hydrochloric acid, sodium chloride and hydrogen peroxide, to convert the platinum metals to the chloride complexes. During the extraction, part of the quadrivalent iridium may be reduced to the tervalent state, so that this operation of evaporating the solution must be repeated before each successive extraction. Moreover, it has been found that the extraction of the chloride complex of rhodium is irreversible, *i.e.*, when the extract is shaken with 1*M* hydrochloric acid no appreciable amounts of rhodium pass into the aqueous phase. To re-extract the rhodium from the organic phase, the extract was shaken with a 25% solution of nitric acid (under these conditions, platinum, palladium and iridium are also re-extracted). The re-extract was then treated with concentrated hydrochloric acid and sodium chloride to reconvert the platinum metals to the chlorides.

The separation was carried out in separating funnels by Bush and Densen's scheme (Fig. 8).[41] A 1% solution of diantipyrylpropylmethane in dichloroethane was used for the extraction. The volume of the organic phase was 10 ml and that of the aqueous phase 20 ml, and the over-all concentration of hydrochloric acid in the aqueous phase was 1*M*. The results obtained are given in Table IX.

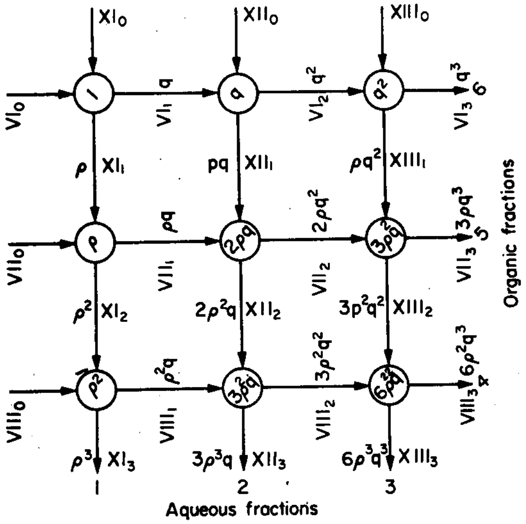


FIG. 8—Scheme of extractive separation.

TABLE IX.—SEPARATION OF RHODIUM AND IRIDIUM, RHODIUM AND PLATINUM, AND RHODIUM AND PALLADIUM

Fraction no.	Metal found,[a] *mg*					
	Rh	Ir	Rh	Pt	Rh	Pd
1	7·60	0·00	7·60	0·00	7·70	0·00
2	2·11	0·00	2·18	0·00	2·12	0·00
3	0·30	0·00	0·18	0·00	0·22	0·00
4	traces	0·000	traces	0·00	traces	0·00
5	0·00	0·33	0·00	traces	0·00	0·32
6	0·00	6·22	0·00	6·50	0·00	7·45

[a] Amounts taken were 9·88 mg of Rh, 6·55 mg of Ir, 6·60 mg of Pt and 7·80 mg of Pd.

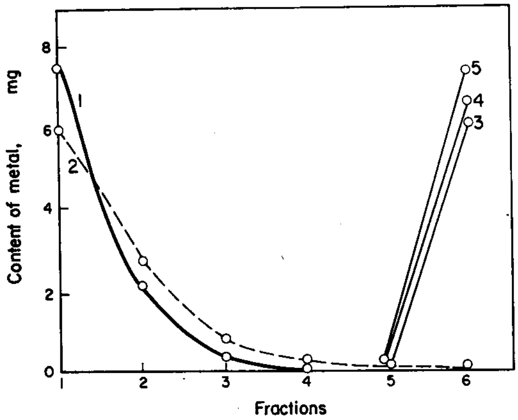


FIG. 9.—Experimental curves of the distribution of rhodium (1), iridium (3), platinum (4) and palladium (5), and theoretical curves of the separation of rhodium (2) and iridium (practically coinciding with the experimental curve).

The experimental distribution curves (Fig. 9) of rhodium and iridium proved to be close to those calculated from the formula

$$p = \frac{K.V_x}{K.V_x + V_y}$$

where p is the fraction of the metal remaining in the aqueous phase after the first extraction, V_x and V_y are the volumes of the aqueous and organic phases, respectively, and $K = \frac{1}{D}$ where D is the distribution coefficient. After a 9-stage extraction separation, about 80% of the original amount of rhodium taken was obtained in the first fraction, which was spectroscopically free from iridium, platinum and palladium. However, to obtain samples of iridium, platinum and palladium spectroscopically free from rhodium it was necessary to carry out the separation with a greater number of extraction stages.

The method developed has been used to purify metallic rhodium from trace amounts of platinum, iridium and palladium.

It is also possible to use diantipyrylpropylmethane for the extractive separation of platinum, palladium, iridium, osmium and ruthenium from other elements, *e.g.* from nickel and selenium, which are not extracted by dichloroethane in the presence of diantipyrylpropylmethane.

Zusammenfassung—Die Reaktion von vierwertigem Osmium und Iridium mit Antipyrin und einigen seiner Derivate wurde untersucht und es wurde gezeigt, daß in sauren Lösungen Verbindugnen vom Typ $(RH)_2MeX_6$ gebildet werden. Die Extraktion von Halogenokomplexen von Osmium, Iridium, Ruthenium, Rhodium, Platin und Palladium mittels Diantipyryl-propylmethan in Dichloräthan wurde geprüft. Eine extraktiv-photometrische Methode wird vorgeschlagen für die Bestimmung von 2–20 μg/ml Osmium neben 50 mg Ruthenium und von 4–40 μg/ml Iridium neben 4 mg Rhodium mittels Diantipyryl-propylmethan. Der Fehler der Bestimmung ist ±10%. Eine gravimetrische Methode zur Osmium- und Iridiumbestimmung, in Mengen von 5–13 mg, mittels Diantipyryl-propylmethan und Diantipyrylmethan wird vorgeschlagen. Die Möglichkeit selektiver Extraktion kleiner Mengen Iridium und Rhodium, Platin und Rhodium und Palladium und Rhodium mittels Diantipyryl-propylmethan wird gezeigt.

Résumé—On a étudié la réaction de l'osmium tétravalent et de l'iridium avec l'antipyrine et quelques-une de ses dérivés, et l'on a montré qu'en solutions acides, il se forme des composés $(RH)_2MeX_6$. On a examiné l'extraction des complexes halogénés d'osmium, iridium, ruthénium, rhodium, platine et palladium au moyen de diantipyrylpropylméthane en dichloréthane. On propose une méthode photométrique par extraction pour le dosage de 2–20 μg/ml d'osmium en présence de 40 mg de ruthénium, et de 4–40 μg/ml d'iridium en présence de 4 mg de rhodium, au moyen de diantipyrylpropyl méthane. L'erreur du dosage est ±10%. On propose une méthode gravimétrique pour le dosage de 5–13 mg d'osmium et d'iridium au moyen de diantipyrylpropylméthane et diantipyrylméthane. L'erreur du dosage est ±3%. On montre la possibilité d'extraire séparément des petites quantités d'iridium et rhodium, platine et rhodium, et palladium et rhodium, à l'aide du diantipyrylpropylméthane.

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Talanta, 1964, Vol. 11, p. 1675. Pergamon Press Ltd. Printed in Northern Ireland

OBITUARY

ELEMÉR SCHULEK

It is with regret that we announce the sudden death on Wednesday, 14th October, 1964, at the age of 71, of ELEMÉR SCHULEK. Professor Schulek, Member of the Hungarian Academy of Sciences and Head of the Institute of Inorganic and Analytical Chemistry of the L. Eötvös University of Budapest, had been a Member of the Advisory Board of *Talanta* since its inception in 1958. A review of his career and his scientific work was published in *Talanta*, 1963, **10**, 429.

Talanta, 1964, Vol. 11, pp. i to iii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

CANADA

Monday 8 *February* 1965: **First Toronto Symposium on Thermal Analysis.** Seaway Towers Hotel, Toronto, Ontario.

The programme will include a technical session, instrument exhibit, dinner and an evening panel discussion between speakers and audience. Papers to be presented will be

Experimental practices and considerations in differential thermal analysis.	P. D. Garn
Dynamic thermogravimetry.	A. E. Newkirk
Quantitative information from DTA.	R. L. Bohon
Making decomposition rate measurements on simple inorganic chemical powders by TGA.	T. R. Ingraham
Simultaneous thermal methods.	W. W. Wendlandt
Applications of thermal analysis to the study of polymers.	H. W. Holden
Application of DTA to evaluation and testing of catalysts.	W. M. Keely
Applications of DTA to petroleum chemistry.	L. Weber

Further details and registration forms may be obtained from Dr. H. G. McAdie, Ontario Research Foundation, 43 Queen's Park Cresent East, Toronto 5, Ontario.

DEUTSCHE DEMOKRATISCHE REPUBLIK

Die Unterkommission für Gas-Chromatographie bei der Sektion Chemie der Deutschen Akademie der Wissenschaften zu Berlin (Sekretariat, Leipzig 0 5, Permoserstraße 15) veranstaltet

vom 11. bis 14. *Mai* 1965 in Berlin
das
V. Symposium über Gas-Chromatographie
in der Deutschen Demokratischen Republik

Es sind Vorträge zur Methodik und Theorie der Gas-Chromatographie, zu vielfältigen anwendungstechnischen und zu apparativen Fragen vorgesehen. In den Nebenräumen des Konferenzsaales wird eine Ausstellung mit kommerziellen Geräten und Zubehör für die Gas-Chromatographie gezeigt werden.

FRANCE

Vendredi 15-1-1965: **Les développements récents de l'électrochimie organique,** par M. G. Cauquis, à 17 h 30, à l'Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre Curie, Paris 5^{e}.

UNITED KINGDOM

Friday 8 *January* 1965: **Annual General Meeting** followed by **Editing a Scientific Journal, J. B.** Attrill: *Society for Analytical Chemistry, Western Section.* College of Advanced Technology, Bristol, 6.30 p.m.

Tuesday 19 *January* 1965: Discussion Meeting on **Analysis of Polyester Resins,** C. H. Hughes: *Society for Analytical Chemistry, Midlands Section.* University of Birmingham, Edgbaston, Birmingham 15, 7.00 p.m.

Friday 22 *January* 1965: **Annual General Meeting:** *Society for Analytical Chemistry, Scottish Section. More's Hotel,* Glasgow, 1.45 p.m.

Wednesday 27 *January* 1965: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemical Methods Group. The Feathers,* Tudor Street, London E.C.4, 6.30 p.m.

Saturday 30 *January* 1965: **Annual General Meeting** followed by address of Retiring Chairman, C. J. House: *Society for Analytical Chemistry, North of England Section. Old Nags Head Hotel,* Lloyd Street, Manchester, 2.15 p.m.

At the *Twentieth Annual General Meeting* of the **Special Techniques Group** of the **Society for Analytical Chemistry** held on Tuesday, 24 November, 1964, the following Officers were elected for the forthcoming year:

Chairman: L. Brealey
Vice-Chairman: G. F. Reynolds
Secretary and Treasurer: T. L. Parkinson, Product Research Department, Beecham Food and Drink Division Ltd., Harpenden Rise, Harpenden, Herts.

British Standards Institution has announced the following *New British Standard: B.S.* 1747*: Methods for the measurement of air pollution: Part* 2*:* 1964*: Determination of concentration of suspended matter.* This covers the construction and use of apparatus for the determination of fine suspended particles (smoke) in the atmosphere, both by comparison with an arbitrary standard and by an absolute (weighing) method. (*Price:* 6s.)

UNITED STATES OF AMERICA

Friday–Saturday 22–23 *January* 1965: **Symposium on Hydrocarbon Analysis—Future Development and Applications:** *American Society for Testing and Materials, Committee D-2 on Petroleum Products and Lubricants.* Sheraton-Lincoln Hotel, Houston, Texas.

The following papers will be presented:

Friday Afternoon, 22 *January—Where we are and a look ahead*

The basis for future developments of hydrocarbon analysis.	S. S. Kurtz, Jr.
Current and future applications of hydrocarbon analysis in quality control.	L. C. Dawson

Potential analytical developments

Mass spectrometric analysis of hydrocarbons.	R. A. Brown and R. F. Stubbeman
NMR analysis of hydrocarbons and related molecules.	J. R. Zimmerman
Absorption spectroscopy of hydrocarbons.	R. L. LeTourneau
Applications of gas chromatography to hydrocarbon analysis.	J. M. Dietz

Saturday Morning, 23 *January—Integrated methods approach*

Gasoline and blended fuels.	D. M. G. Lawrey
Analysis of kerosine and gas-oil fractions.	R. E. Farrell, A. J. Ehrler, I. M. Nawrocka and N. M. Ingber
Aromatic hydrocarbons in high-boiling fractions.	B. J. Mair
The molecular complex comprising heavy petroleum fractions.	J. G. Erdman

Hydrocarbon and non-hydrocarbon impurities

Trace impurities in hydrocarbons used as raw materials.	R. A. Klett, L. R. Korous, R. W. King and R. W. Warren
Sulphur compounds in petroleum.	C. J. Thompson, H. J. Coleman, R. L. Hopkins and H. T. Hall
Basic nitrogen compounds in petroleum.	D. M. Jewell, R. E. Snyder and J. P. Yevich
Non-basic nitrogen compounds in petroleum.	D. R. Latham, I. Okuno and W. E. Haines
Aspects of linear elution adsorption chromatography for extraneous materials.	L. R. Snyder
Research Division IV of Committee D-2 leadership: Past, present and future	J. F. Hickerson

Further information may be obtained from R. R. Wright, A.S.T.M., 1916 Race Street, Philadelphia, Pa. 19103.

Sunday–Friday 16–21 *May* 1965: **13th 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.

In addition to contributed papers, the Conference will include four one-half day symposia in which invited speakers will discuss particular topics. It is expected that over 100 technical papers will be presented during the five day Conference. The general subjects to be covered by the symposia, together with those individuals responsible for their arrangement, are as follows:

Photoionisation and electron impact phenomena:	V. H. Diebler
Isotope abundance and atomic weights:	A. E. Cameron
High resolution mass spectroscopy in organic analysis:	F. W. Lafferty
Instrumentation developments:	W. M. Brubaker

Contributed papers are solicited in research and development topics pertinent to mass spectrometry and ionisation phenomena. The deadline for submitted abstracts is 15 February, 1965. Contributed papers and correspondence should be sent to Dr. H. M. Rosenstock, National Bureau of Standards, Washington, D.C. 20234.

ERRATA—Volume 11

Page 438: The equations should be numbered (1) and (2) and not (2) and (3).
Page 438: In equation (2) [incorrectly numbered (3)] the term $2OH^-$ is unnecessary.
Page 1498, line 2 of the procedure: This should read .....*peroxytitanate, Add potassium*...
Page 1550, line 10 from bottom of page: For *silver-III* read *silver-*111.

Talanta, 1964, Vol. 11, p. iv. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Frontal solubilisation chromatography: HARVEY D. SPITZ, HERBERT L. ROTHBART and WM. RIEMAN III. (8 *October* 1964)

Simultaneous colorimetric determination of thallium^{III} and thallium^{V}: M. H. HASHMI, ABDUR RASHID, HAMID AHMAD and A. A. AYAZ. (14 *October* 1964)

Polarographic study of the uranyl-pyrophosphate complex in the presence of various surface-active substances: TSAI-TEH LAI and SONG-JEY WEY. (16 *October* 1964)

Contributions to the basic problems of complexometry-XVIII: Masking of iron with fluoride: R. PŘIBIL and V. VESELÝ. (16 *October* 1964)

Synthesis of nitrosotirone and the use of some of its colour reactions in analytical chemistry: M. BERAN and S. HAVELKA. (16 *October* 1964)

Photometric determination of niobium with 4-(2-thiazolylazo)resorcinol: VĚNCESLAV PATROVSKÝ. (16 *October* 1964)

The determination of sulphate with barium chloranilate: J. E. BARNEY II. (16 *October* 1964)

Applications of nuclear and electron magnetic resonance in analytical chemistry: A review: B. D. FLOCKHART and R. C. PINK. (19 *October* 1964)

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium-IV: Titrimetric determination of vanadium^{IV} and cerium^{III} alone and in mixtures of iron^{II} with photometric end-points: G. GOPALA RAO and P. KANTA RAO. (19 *October* 1964)

Contribution to the basic problems of complexometry—XIX: Determination of zinc and cadmium: β-Mercaptopropionic acid as a masking reagent for cadmium: R. PŘIBIL and V. VESELÝ. (26 *October* 1964)

Spectrophotometric determination of copper with complexones: 1-Ethylenediamine-*N,N'*-dimethylacetic acid: J. J. R. FRAUSTO DA SILVA, J. C. GONCALVES CALADO and M. LEGRAND DE MOURA. (26 *October* 1964)

Determination of micro-amounts of sulphur in organic substances by a combustion method followed by reduction: TSUGIO TAKEUCHI, IWAO FUJISHIMA and YUZO WAKAYAMA. (27 *October* 1964)

Determination of potassium by a titrimetric method: TADASHI IWACHIDO. (27 *October* 1964)

Chelating resins—their analytical properties and applications: A review: G. SCHMUCKLER. (28 *October* 1964)

Amperometrische Bestimmungsmethode des Thioacetamid (TTA): MARIA PRYSZCZEWSKA. (30 *October* 1964)

Investigation of the behaviour of molybdenum(VI) in formic acid solutions of ion-exchange resins: D. A. SHISHKOV and E. G. KOLEVA. (4 *November* 1964)

Investigation of the behaviour of tungsten(VI) in formic acid solutions of ion-exchange resins: D. A. SHISHKOV and E. G. KOLEVA. (4 *November* 1964)

Investigation of the cation-exchange behaviour of molybdenum(VI) in hydrochloric alcohol solutions: D. A. SHISHKOV and L. G. SHISHKOVA. (4 *November* 1964)

Determination of sulphur chloride by oxidation with chloramine-T: D. K. PADMA and A. R. VASUDEVA MURTHY. (5 *November* 1964)

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PUBLICATIONS RECEIVED

Theorie und Praxis der gravimetrischen Analyse: LÁSZLÓ ERDEY. Band I, Theoretischer Teil, S. 382, \$9.00: Band II, Bestimmung der Kationen, S. 802, \$18.00: Band III, Bestimmung der Anionen, S. 340, \$13.00. Akadémiai Kiadó (Publishing House of the Hungarian Academy of Sciences), Budapest, V, Alkotmány utca 21, Hungary, 1964.

Band I: Einleitung: Qualitative und quantitative Analyse; Die Bedeutung der quantitativen Analyse; Die Eigenart der quantitativen Analyse; Methoden der quantitativen Analyse; Die Menge der analytischen Probe; Das Ziel einer wissenschaftlichen Analyse; Das Ziel der technischen Analysen; Verfahren der Gewichtsanalyse; Fällungsverfahren der Gewichtsanalyse.

Operationen der Gewichtsanalyse: Probenahme und Vorbereitung der Substanz; Die Einwaage der Substanz zur Analyse; Die Auflösung der Probe; Der Aufschluß der Substanz—Hochtenperaturreaktionen; Die praktische Dürchfuhrung des Aufschlusses; Veraschen und Zerstörung organischen Substanzen; Fällung; Das Filtrieren und Auswaschen des Niederschlages; Wärmebehandlung von Niederschlägen; Das Trocknen und Glühen; Auswaage des Niederschlags; Die Berechnung der Ergebnisse der Analyse; Fehler der Analysen.

Trennungsverfahren: Die Trennung durch fractionierte Fällung; Die Trennung mit organischen Reagenzien; Trennung von festung Stoffen durch selektive Auslösung; Die Auslösung mit Hilfe von mit Wasser unmischbaren Lösungsmitteln (Extraktion); Kollektoren; Die Trennung mit Ionaustauscher—Ionenaustausch-Chromatographie; Adsorptions- und Verteilungschromatographie; Papierchromatographie; Die Trennung von flüchtigen Stoffen; Indirekte Analyse; Elektrogravimetrie.

Die Bestimmung des Wassergehaltes von Festen Stoffen; Wasserdampftension; Adsorption des Wassers an der Oberfläche von festen Stoffen; Okklusion des Wassers in der Kristallen; Gravimetrische Bestimmung des Wassers durch thermisches Trocknen; Indirekte Wasserbestimmungsmethoden; Direkte Wasserbestimmung; Weitere Verfahren zur Wasserbestimmung.

Namenverzeichnis.

Sachverzeichnis, 7 S.

Band II: Bestimmung und Trennungsverfahren: Klasse der Kationen; Ag, Pb, Hg, Cu, Bi, Cd: 2. Klasse der Kationen; As, Sb, Sn, Ge, Au, Pt (und die Platinmetalle), Se, Te: 3. Klasse der Kationen; Al, Fe, Cr, Ni, Co, Zn, Mn, Ti, (Zr, Hf), Th (und die seltenen Erden), Sc, (Nb, Ta), Mo, W, V, U, Tl, In, Ga, Be: 4. Klasse der Kationen; Ca, Sr, Ba: 5. Klasse der Kationen; Mg, Na, K, Li, NH_4^+.

Nahmenverzeichnis.

Sachverzeichnis (23 S.)

Band III: Inhaltsverzeichnis zum I Band: Inhaltsverzeichnis zur II Band: Bestimmung und Trennungsverfahren: *Chlor* (Cl_2, HCl, HClO, $HClO_2$, $HClO_3$: *Brom* (HBr, HBrO, $HBrO_3$): *Jod* (J_2, HJ, HJO, HJO_3, JO_4): *Fluor* (F_2, H_2F_2, H_2SiF_6): *Cyanid: Thiocyanat* (*Rhodamid*): *Schwefel* (S_x, $H_2S_2O_3$, $H_2S_2O_4$, H_2SO_4, $H_2S_2O_7$, $H_2S_2O_8$): *Stickstoff* (HNO_2, HNO_3): *Phosphor* (P_x, H_3P, H_3PO_2, H_3PO_3, $H_4P_2O_6$, H_3PO_4, $[HPO_3]_x$, $H_4P_2O_7$): *Kohlenstoff* (C, CO, CO_2, H_2CO_3): *Silicium* (Si, SiO_2, H_2SiO_3): *Bor:* Anhang; Reinigung der bei der Analyse gebrauchten Gefäße; Die zu Analysen benutzten Reagenzien: Die zu Analysen benutzen Gase: Konzentration der Reagenslösungen und der zu bestimmenden Lösungen: Numerische Berechnung der Ergebnisse.

Bibliographie (77 Referate).

Tabellen (Löslichkeitsprodukte der wichtigeren analytischen Niederschläge bei Zimmertemperatur; Stöchiometrische Facktoren; Gekürtze Fünfstellige Logarithmentafel: Interpolationsdiagramm).

Namenverzeichnis.

Sachverzeichnis (7 S.)

The Determination of Sterols: Society for Analytical Chemistry Monograph No. 2. The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1, 1964, pp. 72, 15s: \$2.00.

Six papers originally presented at a Meeting of the Society held on May 2nd 1962.

G. S. BOYD: Determination of cholesterol for clinical purposes. J. GLOVER: Determination of cholesterol and 7-dehydrosterols. C. J. W. BROOKS: Gas-chromatographic examination of sterols. J. H. RECOURT and R. K. BEERTHUS: The detection of animal fats in vegetable fats by gas-chromatographic analysis. W. E. DAVIES, T. W. GOODWIN and E. I. MERCER: The identification and determination of plant sterols. E. V. TRUTER and B. BUSH: Determination of sterols (of wool wax) by the Liebermann-Burchardt reaction. Discussion.

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.

"**Absorption 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 Exchanges in Inorganic Analysis**" by H. Green.

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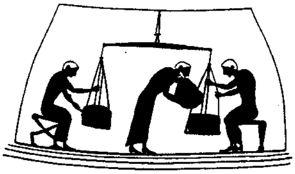

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ERRATA

Volume 10

Page 1088, Table I: For Compound XIII, under the heading *Ar* for *3-Me-4-OH-*C_6H_3 read *3-MeO-4-OH-*C_6H_3.

Page 1088, Table I: For compound *XIII* read *XIV*; for compound *XIV* read *XV*; for compound *XV* read *XIII.*

Volume 11

Page 2, line 7: This should read *Methods have previously been described*...

Page 5: Insert after Zusammenfassung

Résumé—L'utilité analytique particulière de l'Arsenazo-III est due à sa capacité de former des complexes spécialement stables avec certains éléments. Ceci permet le dosage en milieu acide fort (HCl, 10 M ou SO_4H_2) des éléments penta- ou quadrivalents: Pa, Np^{IV}, Th, Zr, Hf, U^{IV}; la reproductibilité est bonne, la manipulation facile et l'on ne note que de petites interférence dûes aux anions. La grande sensibilité (0,1–0,01 μg/ml, coefficient d'absorption molaire $50–150 \times 10^3$) est due au grand effet de contraste de la réaction (changement de coloration du rose au vert émeraude, déplacement du maximum d'absorption de 125 mμ), nature de spectre, et enfin possibilité d'atteindre des dilutions extremes sans dissociation des complexes.

Page 7, line 2 from bottom: For *TR* read *rare earths.*

Page 16, line 2 above formula XIX: This should read *In order to study the formation of complexes by arsenazo III*....

Page 18, line 4 of Synthesis: This should read *excess of nitrous acid*...

Page 41: Insert after Zusammenfassung

Résumé—Les mélanges formés d'orthophosphate, de ses polymères linéares supérieurs jusqu'au tridécaphosphate compris et trois polymères cycliques ont pu être séparés par chromatographie d'échange ionique. L'un des polymères cycliques (recontré dans les verres de polyphosphate... est probablement le pentamétaphosphate. Sa nature cyclique a été démontrée par dosage des groupes terminaux et chromatographie sur papier, mais les tentatives de dénombrement des atomes de phosphore du noyau ont échouées à cause de la très faible quantité de produit disponsible. Évidence est presentée a l'appui de la supposition courante que les phosphates linéaries supérieurs sont élués suivant leur degré de polymérisation.

Page 46: Insert after Zusammenfassung

Résumé—Une méthode pour le dosage des trimétaphosphates en présence d'oligophosphates linéares supérieurs au trimère est developpée. Il a été démontré que l'ortho-, le pyro-, at le triphosphate ne sont pas complètement précipités par l'ion baryum, tandis que les phosphates oligomères linéares de type supérieur sont précipités quantitativement. Ces derniers sont isolés des mélanges de phosphates par chromatographie d'échange d'anions, mélangés avec des quantités connues de phosphates cycliques, et précipités par l'ion baryum. Une erreur moyenne de + 0,8 et un écart standard de ±3 micromoles de phosphore de l'ion cyclique a été mise en évidence dans les mélanges contenant de 0 à 203 micromoles de phosphore sous forme de trimétaphosphate en présence de 0 à 81 micromoles de phosphore sous forme de polymères linéares,

Page 49, line 1: This should read *using barium diphenylamine*. . .

Page 57, line 1: This should read *between ammonium ion and chloramine-T*...

Page 57: Insert after Zusammenfassung

Résumé—La chloramine-T oxyde quantitativement la thiourée en urée et l'ion sulfate en milieu neutre et en millieu basique. L'oxydation est totale en 2 minutes même en présence d'un léger excès d'oxydant. L'urée et l'ion ammonium ne sont pas gênants si l'oxydation est effectuée en milieu alcalin.

Page 105, line 18 of Summary: This should read *Cerfak* [*sodium naphthalene*....

Page 105, line 6 from bottom of page: This should read [*sodium naphthalene*....

Page 271, line 4 of Summary: This should read

$$\textit{by the equations} \qquad \log k = -11{\cdot}372 + 0{\cdot}0128t \qquad \textit{and } \gamma = 45{\cdot}5 - 0{\cdot}182t.$$

Page 288, line 1: This should read $\bar{X} = \Sigma X_i/n$.

Page 288, line 2: This should read *standard error of* $Y_i = \log K_{H_i}$....

Page 290, Fig. 4: This should read ◑ − K_D *in* D_2O.

Page 292, line 4: This should read *than for* D_2O.

Page 1239: This paper should read *Received 18 March 1964.*
Page 1249: This paper should read *Received 9 April 1964.*
Page 1275: This letter should be dated *26 March 1964.*
Page 1284, Fig. 5: This should read $\gamma_0 = 0{\cdot}06$, *etc.*
Page 1307, line 2: For *though* read *through.*
Page 1311, reference 46: This should read . . . *1963,* ***18,*** *18.*
Page 1313, line 4 of Experimental: This should read . . . . *1,2-diaminocyclohexanetetra-acetic.*
Page 1314, line 2 of Apparatus: This should read . . . *photoelectric attachment* . . .
Page 1314, line 4: For UO_2^{2-} read UO_2^{2+}.
Page 1314, line 8 under Results and Discussion: This should read . . . *a molar ratio of 1:1, V:(λ*
Page 1317, Table I: In the first column read UO_2^{2+} for UO_2^{2-}
Page 1325, second footnote to page: Delete *Preparation*:
Page 1329: For *Table 1* read *Table I.*
Page 1350, line 14 of Results and Discussion: This should read . . . *measured in 1-ml cells* . . .
Page 1355, reference 5: The journal should read simply *Japan Analyst.*
Page 1366, line 3 above Procedure: This should read *(1 ml ≡ 100 μg of cadmium).*
Page 1367, line 7 from bottom of page: This should read . . . *chromium(VI), remaining after volatilisation, to chromium(III)* . . . .
Page 1377, line 2 under Calculations: For *MEV* read *MeV.*
Page 1406, Table I: The headings for columns two, three and four should read

Cu^{2+} taken, *mmole/100 ml*	HEDTA taken, *mmole/100 ml*	Resin, *g*

Page 1498, line 2 under the heading *Precipitation of Titanium from Homogeneous Solution:* This should read . . . *peroxytitanate. Add potassium* . . . .
Page 1550, line 10 from bottom of page: For *silver-III* read *silver-111.*
Page 1607, line 8: This should read *hydriodic acid and stannic tetra-iodide* . . . .

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