An International Journal of Analytical Chemistry

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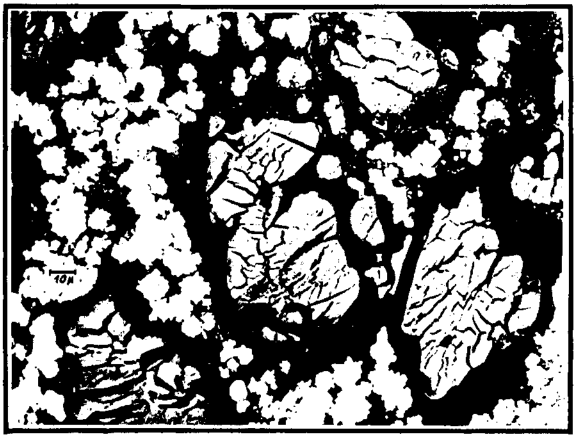

Microphotograph of a DSK working layer.

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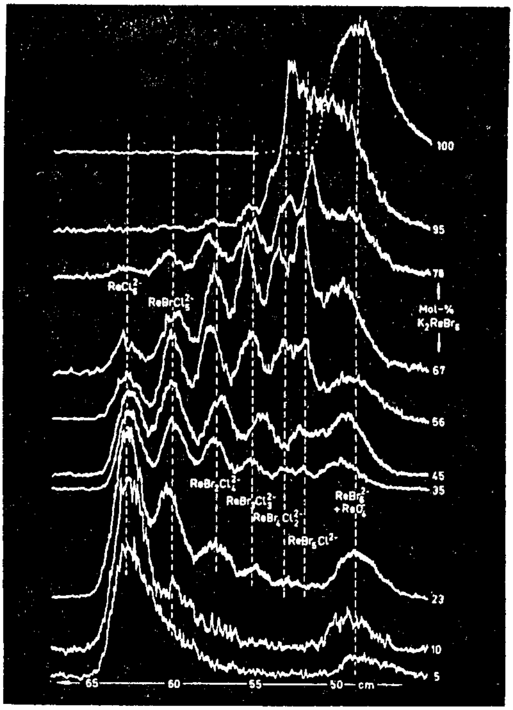
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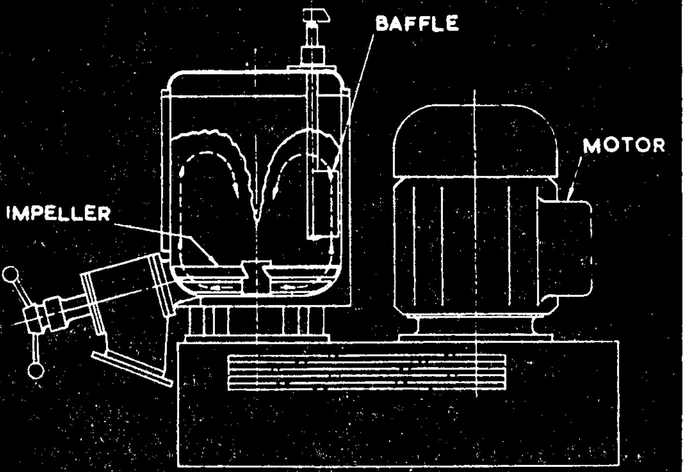
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An International Journal of Analytical Chemistry

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Aims and Scope

Established as a medium for the rapid publication of papers dealing with all aspects of analytical chemistry, *Talanta* is the natural vehicle for the international communication of progress in this field. As an international journal, its papers are expected to be of a very high standard and to make definite contributions to the subject: they must be new publications. Papers may be written in English, French, or German; all papers have abstracts in these three languages and also in Russian. Special importance is attached to work dealing with the principles of analytical chemistry in which experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields or of hitherto widely scattered material are considered for publication, but should be critical. Original papers, short communications and reviews are refereed in the normal manner. Preliminary communications are refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemists is welcomed by the Editor-in-Chief, at whose discretion it is published. A new feature is Annotations, which are critical commentaries on some aspect of analytical chemistry and deal with topics such as sources of error, or the scope and limitations of methods and techniques; these commentaries are refereed.

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LOUIS GORDON MEMORIAL AWARD

THE Editorial Board and the Publisher of TALANTA have great pleasure in announcing that the Louis Gordon Memorial Award for 1969, for the best-written paper published that year in TALANTA, has been made to Dr. S. J. Lyle and Mr. V. C. Nair, of the University of Kent, for their paper on "Reversed-Phase Partition Chromatographic Separations with 2-Ethylhexyl Dihydrogen Phosphate and Di-2-Ethylhexyl Hydrogen Phosphate", *Talanta*, 1969, **16,** 813.

DR RUDOLF PŘIBIL

DR. RUDOLF PŘIBIL

DR. RUDOLF PŘIBIL, who is the senior research chemist of the Polarographic Institute of the Czechoslovak Academy of Sciences, attains his 60th birthday this year. Dr. Přibil was born on 23 July 1910, in Prague. He studied chemistry, mathematics and physics at Charles University in Prague, his interest being concentrated mostly on analytical chemistry. He received the degree of Doctor of Natural Sciences in 1933. He continued to work under Prof. O. Tomíček as an assistant in the Institute of Analytical Chemistry in the Faculty of Natural Sciences at Charles University until the second World War. When the University was closed by the Germans, Dr. Přibil worked in a chemical factory in Rybitví as a research analyst. After the war Dr. Přibil turned his attention to the rebuilding of the Institute of Analytical Chemistry at Charles University.

In 1946 he made his "habilitation" in the field of analytical chemistry and continued as the assistant of Prof. O. Tomíček. In 1948–1950 Dr. Přibil was head of the Institute of Inorganic and Forensic Chemistry in the Faculty of Natural Sciences at Charles University. At the same time he continued teaching in the Institute of Analytical Chemistry. In 1950 he left the University to act as head of the Division of Analytical Chemistry in the Institute for Pharmacy and Biochemistry, where he worked until 1955. From 1955 Dr. Přibil worked in the Czechoslovak Academy of Sciences as a research worker and in 1958 became head of the Laboratory of Analytical Chemistry.

Influenced by his teacher Prof. O. Tomíček, Rudolf Přibil began his research activity in the field of potentiometry. After World War II he turned his interest to the application of complex-forming substances in analytical chemistry. In the series of papers written by G. Schwarzenbach and describing the properties of some polyaminopolycarboxylic acids he recognized the role which these compounds may play in analytical methods. In 1947 he started a systematic study devoted to the application of EDTA in gravimetry, colorimetry, polarography, and solvent extraction. Since 1953 he has studied chelometric titration with EDTA and classical chelometric indicators. He was mostly interested in the problem of increasing the selectivity of chelometric titrations, and successfully applied the masking properties of triethanolamine, fluoride and various thio-compounds, in EDTA titrations.

In 1956 Přibil published his first paper devoted to a new type of metallochromic indicator—on Xylenol Orange. These indicators of phthalein and sulphophthalein type were (and still are) very suitable for EDTA titrations and are now manufactured all over the world. Přibil's paper influenced the other analysts to begin research work in this field and thus EDTA titrations became a new branch of modern volumetric analysis.

In the sixties Přibil studied mostly the chelometric determination of rare earths, zirconium *etc*, and on the basis of his experience in chelometry developed a series of methods for the analysis of various industrial materials. Recently he has studied the possibility of the application of metallochromic indicators in spectrophotometry and in extraction colorimetry.

Dr. Přibil has published about 250 papers and 15 monographs. He was awarded the State Prize for chemistry in 1953 and in 1958 received the academic degree of

Doctor of Science. He has been a Regional Editor of *Talanta* since its inception in 1958. As a lecturer or visiting professor he has visited many research institutions and universities in Europe, America and Asia. Due to his personal charm and social activity he has thus found a lot of friends throughout the world. All his friends, students and co-workers wish him much health and personal success.

Long life to our Rudla!

M. KOPANICA

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KOMPLEXE DER ANTHRANIL-*N*,*N*-DIESSIGSÄURE MIT METALLEN IN DER OXYDATIONSSTUFE +4—I

ZIRKONIUM UND HAFNIUM

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(*Eingegangen am* 31. *Juli* 1968. *Revidiert am* 25. *Octobre* 1969. *Angenommen am* 31. *Januar* 1970)

Zusammenfassung—Spektrophotometrische Untersuchungen zeigten, daß Zirkonium und Hafnium mit Anthranil-*N*,*N*-diessigsäure (ANDA) in wäßriger Lösung Komplexe der Zusammensetzungen Me:ANDA = 1:1 und 1:2 bilden. Die stufenweisen Bildungskonstanten bei pH 1 betragen für Zirkonium $k_1 = 20 \pm 5$ und $k_2 = 1{,}42 \cdot 10^5$, für Hafnium $k_1 = 10 \pm 5$ und $k_2 = 1{,}22 \cdot 10^5$.

Die chelatisierende Wirkung der Anthranil-*N*,*N*-diessigsäure (ANDA) auf eine Anzahl Metalle in der Oxydationsstuf +2, +3 und +4 wurde in früheren Arbeiten behandelt.[1] Aufbauend auf die Spektrophotometrie farbloser Me–ANDA-Komplexe[2] werden in der vorliegenden Arbeit die Ergebnisse einer UV-Untersuchung der durch ANDA mit Zirkonyl- und Hafnylionen gebildeten Komplexe aufgezeigt. Durch Ermittlung der Zusammensetzung und Stabilität der gebildeten Komplexe sollen Bedingungen erarbeitet werden, unter denen die photometrische Bestimmung von Hafnium in Gegenwart von Zirkonium möglich ist.

EXPERIMENTELLER TEIL

Apparate

Die Absorptionskurven im UV-Bereich wurden mit dem automatischen Spektrophotometer Unicam SP 800 aufgenommen. Alle Absorptionsmessungen wurden mit einem VSU 1 C. Zeiss (Jena, DDR)-Spektrometer durchgeführt. Die Schichtdicken der verwendeten Küvetten sind in der Zeichenerklärung der betreffenden Abbildungen angegeben. Sofern keine anderen Angaben gemacht wurden, diente als Bezugsflüssigkeit bidestilliertes Wasser. Die pH-Werte der Lösungen wurden mit einem pH-Meter Typ MV 11 Clamann und Grahnert (Dresden, DDR) bestimmt.

Reagenzien

Zur Herstellung der $5 \,.\, 10^{-3}M$-Lösung des Dinatriumsalzes der Anthranil-*N*,*N*-diessigsäure wurden 1,2654 g synthetisiertes ANDA[3] in 2 Äquivalentgramm Natrium hydroxid gelöst, wobei bidestilliertes Wasser bis zu 1 Litre hinzugefügt wurde. Der Titer der stabilen Lösung wurde komplexometrisch bestimmt.[3]

Zirkonylchlorid. Die entsprechende Menge $ZrOCl_2.8H_2O$ (Loba-Chemie Fischamend, Wien, *p.a* oder Johnson Matthey "Specpure") wurde in $10^{-1}M$ Perchlorsäure gelöst. Das verwendete Zirkonylchlorid war nicht hafniumfrei. Die Bestimmung von Zirkonium wurde gravimetrisch durchgeführt.

Hafniumchlorid. Die entsprechende Menge metallisches Hafnium "Spectral rein" wurde in konzentrierter Salszäure *p.a.* unter Zusatz einiger Tropfen konzentrierten Fluorwasserstoffs *p.a.* gelöst. Anschließend wurde das Hydroxid mit Ammoniak gefällt und bis zur negativen Reaktion auf Chlorid gewaschen. Die Auflösung des Hafniumhydroxid geschah in der kleinsten Menge warmer Salzsäure und die Ergänzung bis zur Marke mit $10^{-1}M$ Perchlorsäure. Zur Bestimmung der Bildungskonstanten wurde Hafniumoxidchlorid (Johnson Matthey "Specpure", London) verwendet.

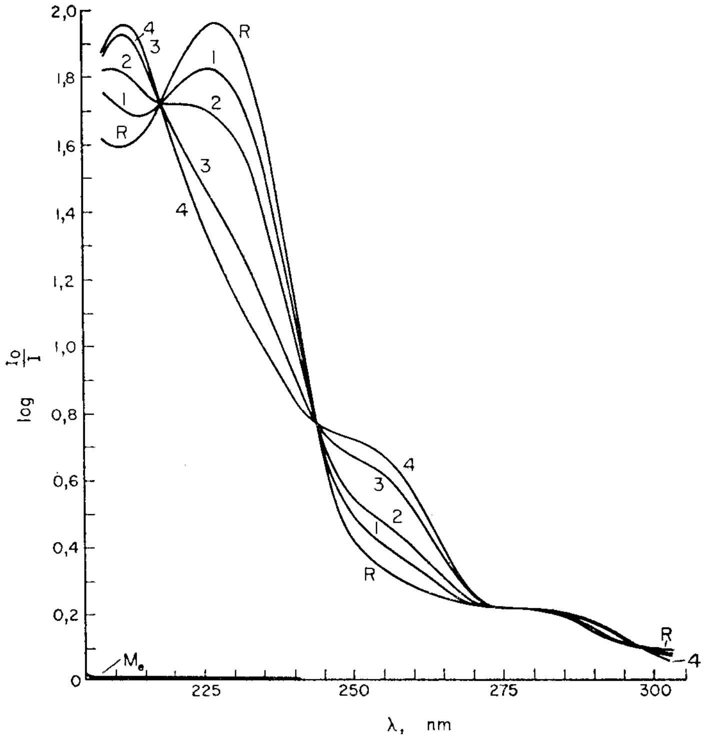
Natriumperchlorat (VEB Laborchemie Apolda, DDR). Zwecks Bestimmung der Bildungskonstanten wurde eine $1M$ Natriumperchlorat-Lösung in Wasser bzw. in $10^{-1}M$ Perchlorsäure benutzt.

Das bei sämtlichen Untersuchungen verwendete Lösungsmittel war eine $10^{-1}M$ Perchlorsäurelösung.

ERGEBNISSE UND DISKUSSION

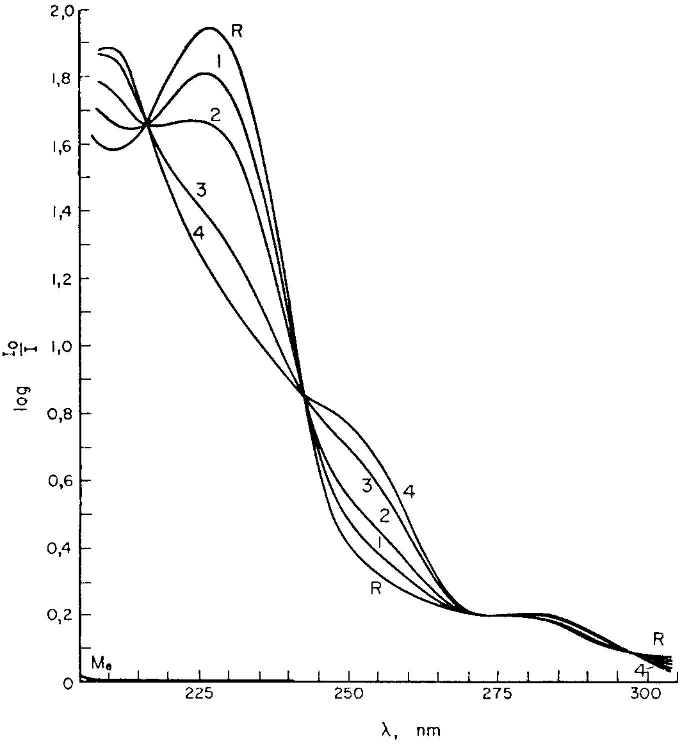
Die Reaktionen, die zwischen Anthranildiessigsäure und Zirkon- bzw. Hafniumoxidchlorid stattfinden, treten durch Vergleich der Form der Absorptionskurven der Verbindung Zr-ANDA (Abb. 1A, Kurven *1* bis *4*) bzw. Hf-ANDA (Abb. 1B, Kurven *1* bis *4*) mit denen der Reaktanten (Kurven *R* und *Me*) hervor. Die Abbildungen zeigen die starke Absorption des Liganden in diesem Spektralbereich sowie die Ähnlichkeit, die zwischen den Kurven der beiden Reaktionsprodukte ohne charakteristische Absorptionsbanden besteht.

Um den optimalen pH-Wert der Komplexbildungsreaktion zu finden, wurden die Absorptionskurven der Zr-, Hf-ANDA-Komplexe bei unterschiedlichen pH-Werten aufgetragen. Die Wahl der pH-Werte ist einerseits durch die Fällungsmöglichkeit des Liganden, andererseits durch die Hydrolyse des MeO^{2+}-Ions begrenzt. Abbildung 2 zeigt für die Reaktion zwischen ZrO^{2+} und ANDA durch die Bildung des isosbestischen Punktes das Vorhandensein eines Gleichgewichts bei den pH-Werten zwischen 0, 7 und 2. Bei höheren pH-Werten (Kurve *4*, pH = 3) liegt kein Gleichgewicht mehr vor. Der Hf-ANDA-Komplex verhält sich ähnlich. Der optimale pH-Wert für beide Systeme beträgt 1. Er wird mit Hilfe einer $10^{-1}M$ Perchlorsäurelösung erhalten.



1A

Abb. 1.—Absorptionskurven des Systems Zr-ANDA (Diagramm A) und Hf-ANDA (Diagramm B)
Konstante Ligandkonzentration: $1{,}2 \cdot 10^{-3}M$. Kationenkonzentration: 0 (Kurve *R*), $1 \cdot 10^{-4}M$ (Kurve *1*), $2 \cdot 10^{-4}M$ (*2*), $3 \cdot 10^{-4}M$ (*3*), $4 \cdot 10^{-4}M$ (*4*),$5 \cdot 10^{-4}$ *M* (*5*).
Bezugslösung: bidestilliertes Wasser. Schichtdicke 2 mm.



1B

Die zeitliche Verfolgung der Bildung der Zr-, Hf-ANDA-Komplexe in Abhängigkeit vom pH-Wert ergibt, daß die Reaktion bei pH-Werten zwischen 1 und 3 praktisch augenblicklich stattfindet und die gebildeten Komplexe wenigstens 3 Stunden stabil sind.

Die Ionenstärke der Lösungen wird mit Hilfe einer 1*M* Natriumperchloratlösung bei einem Wert $\mu = 0,25$ konstant gehalten.

Natur und Zusammensetzung der Zr-, Hf-ANDA-Komplexe

Es werden die Absorptionskurven für eine Reihe von Lösungen aufgenommen, in denen die Menge des Liganden konstant, die Menge des Metallions hingegen veränderlich ist. Für den Zr-ANDA-Komplex erhält man Diagramm A, für den Hf-ANDA-Komplex Diagramm B in Abb. 3.

Die Bildung der isosbestischen Punkte zwischen der Kurve des reinen Liganden (*1*) und den Kurven der Komplexe bis zum Erreichen des Verhältnisses Me:ANDA = 1:2 (Kurve *4* in Diagramm A und *5* in B) weist auf das Bestehen eines Gleichgewichts zwischen dem Me-$(ANDA)_2$-Komplex und dem Ligandüberschuß hin. Ebenfalls bringt die Unmöglichkeit, Gleichgewichte bei einem Überschuß an Metallionen zu erkennen (Kurven *7* bis *9*), die Tatsache zum Ausdruck, daß die Zr-, Hf-ANDA-Systeme keine polynuklearen Komplexe bilden.

Die beiden isosbestischen Punktpaare zeigen für die zwei Systeme Zr-$(ANDA)_2$ und Hf-$(ANDA)_2$ eine geringe Wellenlängenverschiebung. Die isosbestischen Punkte im

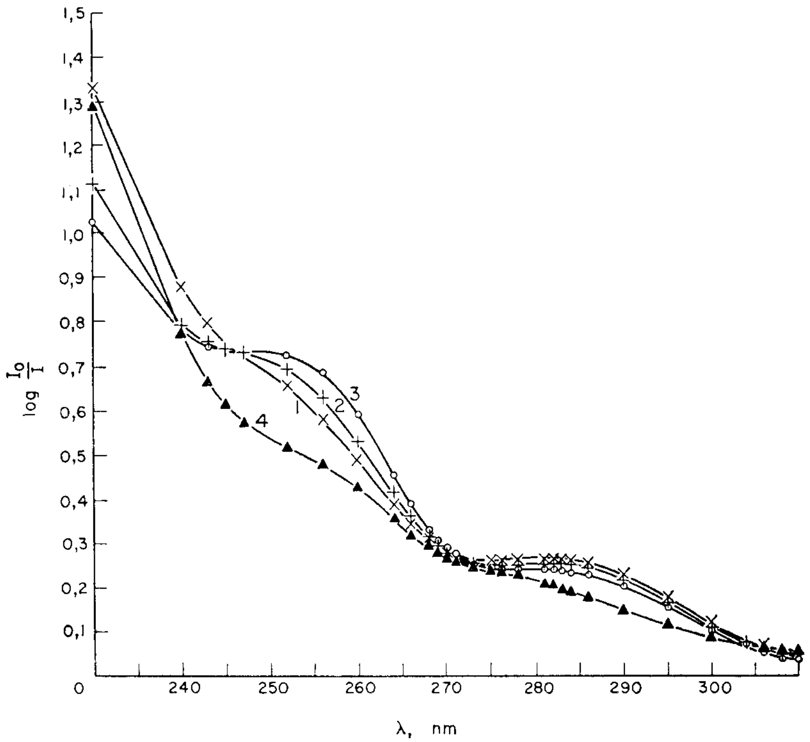


Abb. 2.—Absorptionskurven des Zr-ANDA-Komplexes mit der Konzentration $2 . 10^{-4}M$ bei unterschiedlichen pH-Werten.
Kurve *1* für pH 6 = 0,7; Kurve *2*, pH = 1; Kurve *3*, pH = 2 und Kurve *4*, pH = 3.
Schichtdicke 20 mm.

Bereich kleinerer Wellenlängen sind für den Zr-ANDA-Komplex λ_{iso} mit ungefähr 243,5 nm und für den Hf-ANDA-Komplex λ_{iso} mit ungefähr 242,5 nm gleich. Beim λ_{iso} des $Zr(ANDA)_2$-Komplex weist der Hf-$(ANDA)_2$-Komplex eigene Absorption auf. Diese Tatsache macht bei dieser Wellenlänge die Bestimmung von Hafnium in Gegenwart von Zirkonium unter der Bedingung möglich, daß das Verhältnis Me:ANDA = 1:2 eingehalten wird.[4] Die beiden anderen isosbestischen Punkte der betrachteten Systeme im Bereich größerer Wellenlängen (ungefähr 300 nm für den Zr-$(ANDA)_2$-Komplex und 297 nm für den Hf-$(ANDA)_2$-Komplex) bringen grundsätzlich die spektrophotometrische Bestimmungsmöglichkeit von Zirkonium in Gegenwart von Hafnium bei λ_{iso} des Hf-$(ANDA)_2$-Komplexes zum Ausdruck.

Der spektrophotometrische Beweis für das Vorhandensein eines 1:1 Komplexes, dessen Bildung wahrscheinlich ist, läßt sich durch eine graphische Erweiterung von Abb. 3 führen. Da das registrierende Spektrophotometer zu gedrängte Kurven liefert, wurden manuelle spektrophotometrische Messungen gemacht und die Kurven für den Zr-ANDA-Komplex in vergrößertem Maßstab in Abb. 3, AI und II eingetragen. Auf diese Weise werden noch zwei weitere isosbestische Punkte bei ungefähr 253 nm (Abb. 3AI) und 268 nm (Abb. 3AII) erhalten, die einem Gleichgewicht zwischen den Komponenten mit den Verhältnissen Me:ANDA > 1:2 (Kurve mit dem Symbol ▲ in Abb. 3AI, II) und dem Metallionüberschuß (Kurve ○) entsprechen.

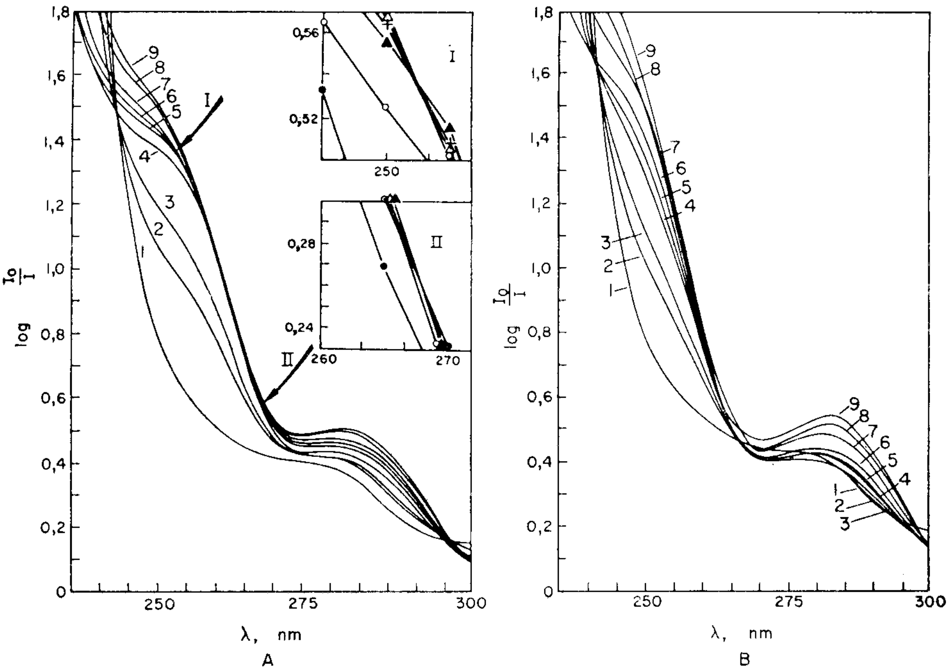


Abb. 3.—Absorptionskurven der Zr-ANDA-(Diagramm A) und Hf-ANDA (B)-Verbindungen.
Konstante Konzentration des Liganden: $2 \,.\, 10^{-4}M$. Konzentration MeO^{2+} für das Diagramm A: 0 (Kurve *1*); $0{,}4 \,.\, 10^{-4}M$ (*2*); $0{,}6 \,.\, 10^{-4}M$ (*3*); $1 \,.\, 10^{-4}M$ (*4*); $1{,}2 \,.\, 10^{-4}M$ (*5*); $1{,}5 \,.\, 10^{-4}M$ (*6*); $2 \,.\, 10^{-4}M$ (*7*); $10 \,.\, 10^{-4}M$ (*8*); $30 \,.\, 10^{-4}M$ (*9*); für das Diagramm B: 0 (Kurve *1*); $0{,}4 \,.\, 10^{-4}M$ (*2*); $0{,}6 \,.\, 10^{-4}M$ (*3*); $1 \,.\, 10^{-4}M$ (*4*); $1{,}2 \,.\, 10^{-4}M$ (*5*); $1{,}5 \,.\, 10^{-4}M$ (*6*); $2 \,.\, 10^{-4}M$ (*7*); $20 \,.\, 10^{-4}M$ (*8*); $30 \,.\, 10^{-4}M$ (*9*). Schichtdicke: 20 mm.
Für Diagramm A I und II ist die Konzentration des Liganden konstant $= 1{,}6 \,.\, 10^{-4}M$ und die des ZrO^{2+} Ions veränderlich: $4 \,.\, 10^{-5}M$ (●); $8 \,.\, 10^{-5}M$ (○); $1{,}2 \,.\, 10^{-4}M$ (▼); $1{,}6 \,.\, 10^{-4}M$ (×); $2 \,.\, 10^{-4}M$ (△); $6{,}4 \,.\, 10^{-4}M$ (⊙). Schichtdicke: 10 mm.

Unter der Annahme, daß sich Hafnium analog verhält, kann demnach gesagt werden:

(*a*) In den zwei untersuchten Me-ANDA-Systemen liegen keine polynuklearen Komplexe vor;

(*b*) die Komplexbildung findet nacheinander in zwei Schritten statt (Verbindung 1:1 und 1:2).

Obwohl bekannt ist, daß eine Anzahl spektrophotometrischer Methoden zur Bestimmung der Komplexzusammensetzung nur bei der Bildung eines einzigen Komplexes gültig ist, wurde geprüft, bis zu welchem Ausmaß die Komplexzusammensetzung der untersuchten Systeme mit Hilfe dieser Methoden ermittelt werden kann. Auf diese Weise kamen zur Anwendung:

Methode des isosbestischen Punktes nach Asmus[5]

Im Falle der Zr-, Hf-ANDA-Komplexe (Abb. 4) zeigt die Überschneidung der Tangenten für den Molenbruch 0,65 das Verhältnis Zr, Hf:ANDA = 1:2, ohne

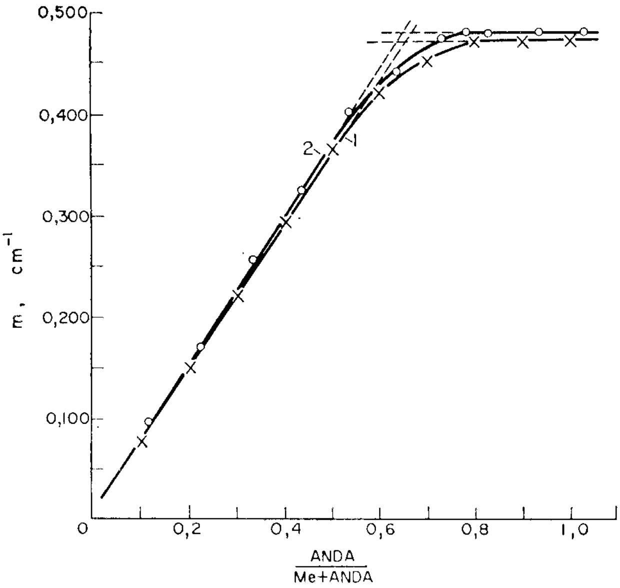


ABB. 4.—Methode des isobestischen Punktes für den Hf-ANDA-Komplex, (Kurve *1*) und den Zr-ANDA-Komplex (Kurve *2*).
$\lambda = \lambda_{iso} = 247,5$ nm für Kurve *1* und 273 nm für Kurve *2*. Konzentration der Proben $2 . 10^{-4}M$. Schichtdicke: 20 mm.

dabei den geringsten Hinweis auf das Vorliegen der betreffenden 1:1-Komplexe zu geben.

Methode der molaren Verhältnisse[6]

Im Falle der Zr-ANDA- und Hf-ANDA-Komplexe weist die Methode auf die Bildung einiger Me-ANDA-Verbindungen mit der Zusammensetzung 1:2 hin.

Demnach ergibt sich: Unter der Bedingung, daß mehrere Komplexe vorhanden sind, die im selben Spektralbereich absorbieren, geben die erhaltenen Ergebnisse nicht den wirklichen Zustand der untersuchten Zr-, Hf-ANDA-Systeme wieder. Weiterhin ist anzunehmen, daß der Bildungsgrad des Komplexes mit der Zusammensetzung 1:1 geringer ist als derjenige mit der Zusammensetzung 1:2.

Stabilität der Zr-, Hf-ANDA-Komplexe

Um die aufeinanderfolgenden Bildungskonstanten der beiden Systeme zu berechnen, wurde die spektrophotometrische Methode nach Newman und Hume[7] angewendet. Aus Abb. 3 ist ersichtlich, daß bei der Wellenlänge der isosbestischen Punkte, die die Komplexe Me:ANDA = 1:2 kennzeichnet, die Komplexe mit der Zusammensetzung 1:1 eine veränderliche Absorption aufweisen. Es ist demnach vorteilhaft, bei $\lambda =$ 243 nm für den Zr-ANDA-Komplex bzw. bei $\lambda = 242$ nm für den Hf-ANDA-Komplex oder bei angenäherten Wellenlängen zu arbeiten. Es wurde bei konstanter Ionenstärke in $2 \cdot 10^{-1}M$ Natrium perchlorat lösung gearbeitet.

Wenn das Verhältnis der beiden aufeinanderfolgenden Konstanten k_2/k_1 genügend groß ist, kann man die Bildungskonstante k_1 in Gegenwart eines Überschußes von

Metallionen (M_t) gegenüber dem Liganden (X_t) bestimmen. Ein Metallionenüberschuß ist außerdem wegen der Absorption des Liganden im gesamten Absorptionsbereich beider Systeme vorteilhaft.

Für die Metallionenkonzentration $6 \,.\, 10^{-3} M$ und die Ligandenkonzentration $8 \cdot 10^{-5} M$ wurde der molare Extinktionskoeffizient aus der Beziehung $E_1 = A_0''/X_0$ berechnet. (A_0'' = gemessene Absorption des ersten Komplexes; X_0 = Ligandenkonzentration). Für den Hf-ANDA-Komplex wurde $E_1 = 4{,}25 \times 10^3$ berechnet.

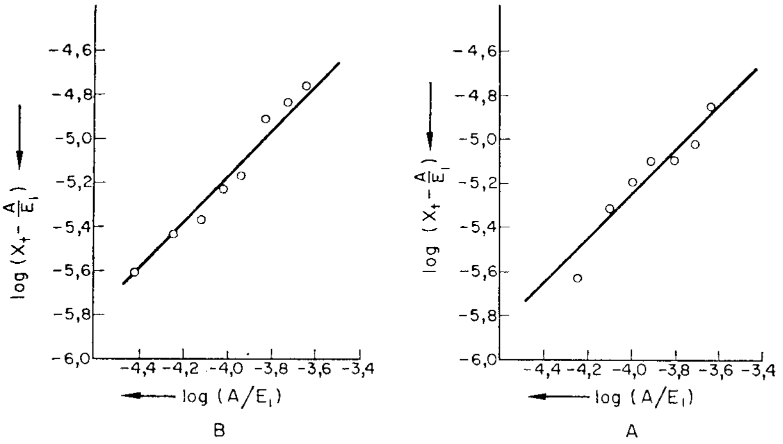


ABB. 5.—Bestimmung der ersten Bildungskonstante des Zr-ANDA-Komplexes (A), bzw. des Hf-ANDA-Komplexes (B).
Konstante Konzentration von $MeOCl_2$ $10^{-3}M$; veränderliche Konzentration von ANDA im Bereich von $4 \,.\, 10^{-5}M$ bis $24 \,.\, 10^{-5}M$. $\lambda = 243$ nm (A) bzw. 242 nm (B). Bezugslösung: Maßlösung ohne ANDA. Schichtdicke: 10 mm.

Im Falle der weiter oben erwähnten Bedingungen wurde die Beziehung (Gleichung F19 von Newman und Hume.[7])

$$\log \left(\frac{A}{A_0''} X_0 \right) = q \left\{ \log \left(X_t - q \frac{A}{A_0''} X_0 \right) \right\} + \log k_1$$

angewendet. Es wurde weiterhin angenommen, daß zwei Komplexe vorhanden sind, von denen einer absorbiert, daß $[MX_2] = 0$, und daß E (der molare Extinktionskoeffizient des Metallions) gleich Null ist. Der Koeffizient q, mit welchem der Ligand an der Reaktion teilnimmt, wird für diesen Fall gleich 1 gesetzt. Indem das linke Glied der Gleichung in Abhängigkeit vom Ausdruck in der geschweiften Klammer graphisch dargestellt wird, werden die Geraden in Abb. 5 erhalten, und zwar A im Falle des Zr-ANDA-Komplexes und B im Falle des Hf-ANDA-Komplexes. Die mit 1 gleiche Neigung bestätigt die gute Wahl des Wertes q.

Aus dem Schnittpunkt mit der Abszisse wurde die erste Bildungskonstante $k_1 = 20 \pm 5$ für den Zr-ANDA-Komplex (bei $\lambda = 243$ nm) und $k_1 = 10 \pm 5$ für den Hf-ANDA-Komplex (bei $\lambda = 242$ nm) erhalten. Wie die Konstanten erkennen lassen, bilden sich Verbindungen mit sehr geringer Stabilität. Die Hafniumverbindung ist verhältnismäßig unstabiler als die Zirkoniumverbindung.

Um die zweite Bildungskonstante zu ermitteln, hätten zwei Wege eingeschlagen werden können. Man hätte den zweiten niedrigen Komplex berechnen können, wobei der vorhin bestimmte Wert für k_1 zu beachten gewesen wäre, oder es hätte das

Endglied in der Reihe der sukzessiven Komplexe berechnet werden können. Die letzte Alternative besitzt den Vorteil, nicht an die Fehler gebunden zu sein welche die Bestimmung der ersten Konstante begleiten. Sie fordert jedoch für die Berechnung von E_n, den molaren Extinktionskoeffizienten des Komplexes mit der maximalen Koordinationszahl, die Verwendung eines großen Ligandüberschusses. Da der Ligand im gesamten Wellenbereich, in dem die Komplexe absorbieren, ebenfalls stark absorbiert, ist dieser Weg nicht gangbar. Deshalb wurde zur Berechnung von k_2 für beide Zr-, Hf-ANDA-Systeme eine modifizierte Form der Newman und Hume D9-Gleichung benutzt:

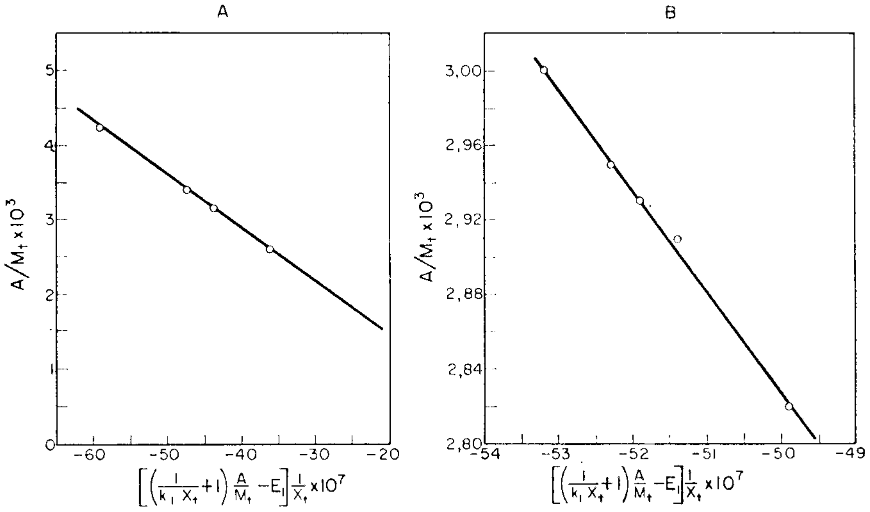


ABB. 6.—Bestimmung der zweiten Bildungskonstante des Zr-ANDA-Komplexes (Diagramm A) und des Hf-ANDA-Komplexes (Diagramm B). Konstante Konzentration von ANDA 6 . $10^{-4}M$ = veränderliche Konzentration von MeO^{2+} im Bereich von 4 . $10^{-5}M$ bis 24 . $10^{-5}M$; $\lambda = 253$ nm (A) und 250 nm (B). Bezug = Meßlösung ohne MeO^{2+}. Schichtdicke: 10 mm.

$$\frac{A}{M_t} = -\frac{1}{k_2}\left\{\left[\left(\frac{1}{k_1 x_t} + 1\right)\frac{A}{M_t} - E_1\right]\frac{1}{x_t}\right\} + E_2$$

Diese Gleichung entspricht den Eigenschaften der in Betracht gezogenen Systeme. Bei der Bestimmung der Bildungskonstante des zweiten Komplexes der beiden Systeme wurde bei der Wellenlänge des isosbestischen Punktes der betreffenden äquimolaren Komplexe oder bei λ-Werten, die diesen sehr angenähert waren, gearbeitet. Im Falle des Zr-$(ANDA)_2$-Komplexes wurden die Bestimmungen bei $\lambda = 253$ nm und im Falle des Hf-$(ANDA)_2$-Komplexes bei $\lambda = 250$ nm ausgeführt. Auch in diesem Fall wurde in einer $2 \cdot 10^{-1}M$ Natriumperchloratlösung gearbeitet.

Trägt man aus obiger Gleichung A/M_t gegen den Ausdruck in der geschweiften Klammer auf, so erhält man Geraden. Diagramm A gilt für den Zr-$(ANDA)_2$-Komplex und B für den Hf-$(ANDA)_2$-Komplex. Aus der Neigung wurde die Konstante $k_2 = 1{,}42 \cdot 10^5$ für Zr-$(ANDA)_2$ und $k_2 = 1{,}22 \cdot 10^5$ für Hf-$(ANDA)_2$ berechnet. Wie die Größe der k_2-Konstanten erkennen läßt, bilden sich Me-$(ANDA)_2$-Komplexe von mittlerer Stärke.

Als globale Bildungskonstante erhält man für das Zr-ANDA-System $K = k_1 \times k_2 = 2{,}80 \cdot 10^6$ und für das Hf-ANDA-System $K = 1{,}2 \cdot 10^6$.

Summary—Spectrophotometric studies have shown that zirconium and hafnium form complexes with anthranil-*N*,*N*-diacetic acid (ANDA) in aqueous solution, with the compositions Me:ANDA 1:1 and 1:2. The conditional stepwise formation constants at pH 1 were found to be $k_1 = 20 \pm 5$ and $k_2 = 1{\cdot}42 \times 10^5$ for zirconium, and $k_1 = 10 \pm 5$ and $k_2 = 1{\cdot}22 \times 10^5$ for hafnium.

Résumé—Des études spectrophotométriques ont montré que le zirconium et le hafnium forment des complexes avec l'acide anthranil-*N*,*N*-diacétique (ANDA) en solution aqueuse, avec les compositions Me:ANDA 1:1 et 1:2. On a trouvé que les constantes de formation étagée à pH 1 sont $k_1 = 20 \pm 5$ et $k_2 = 1{,}42 \times 10^5$ pour le zirconium et $k_1 = 10 \pm 5$ et $k_2 = 1{,}22 \times 10^5$ pour le hafnium.

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GLEICHZEITIGE SPEKTROPHOTOMETRISCHE BESTIMMUNG DES ZIRKONIUMS UND HAFNIUMS

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Zusammenfassung—Zirkonium kann in Gegenwart von Hafnium ultraviolettspektrophotometrisch bei den isosbestischen Wellenlängen 218,2; 243,5 oder 298,5 nm mit Anthranil-*N*,*N*-diessigsäure in verdünnter saurer Lösung bestimmt werden. Konzentrationen im Bereich 2–36 μg/ml (Zr) und 3–70 μg/ml (Hf) können bestimmt werden. Liegen beide Elemente vor, so können 2,5–80% Zr in Hf oder umgekehrt mit einem Fehler von 3–4% bestimmt werden.

ANTHRANIL-*N*,*N*-DIESSIGSÄURE (ANDA) bildet mit den Ionen ZrO^{2+} und HfO^{2+} Chelatkomplexe. Hierüber wurde schon in einer früheren Arbeit[1] berichtet. Untersuchungen über die Gleichgewichte mit Hilfe der Methode des isosbestischen Punktes zeigten eine kleine Verschiebung der Lage der isosbestischen Punkte der beiden Systeme $Zr\text{-}(ANDA)_2$ und $Hf\text{-}(ANDA)_2$. Diese Tatsache läßt sich zur Bestimmung von Zirconium in Gegenwart von Hafnium und umgekehrt ausnutzen.

ERGEBNISSE UND DISKUSSION

Die Absorptionskurven für die Komplexe Zr-ANDA und Hf-ANDA bei konstanter Ligandmenge, bei einem Ligandüberschuß und bei steigender Kationenmenge zeigt Abb. 1 Diagramm A und B in Citat 1. In beiden Fällen bilden sich je drei isosbestische Punkte. Sie liegen für den Komplex Zr-ANDA bei ungefähr 218 nm, 243,5 nm und 298 nm, für den Komplex Hf-ANDA aber bei ungefähr 216,5 nm, 242,5 nm und 297 nm. Diese isosbestischen Punkte bleiben bis zu einem Verhältnis Me:ANDA = 1:2 bestehen.

Nachher weisen die entsprechenden Punkte Extinktionen auf, die mit der anwesenden Kationenmenge steigen. Somit muß eine Ligandmenge eingesetzt werden, die ein Verhältnis Me:ANDA = 1:2 sichert. Außerdem bedingt der mittlere Wert der Komplexstabilitätskonstanten die Verwendung eines Ligandüberschusses, damit eine vollständige Komplexierung der Kationen erreicht wird. In den isosbestischen Punkten (siehe Abb. 1) haben alle Kurven von *R* (Eichkurve des reinen Liganden) bis zu Kurve *4* dieselbe Extinktion. Betrachtet man für beide Systeme je zwei isosbestische Punkte aus demselben Wellenlängenbereich, so ergibt sich:

(*1*) Bei 218 nm besitzt das System Zr-ANDA eine Extinktion, die konstant und gleich ist der des Liganden. Demgegenüber weist aber das System Hf-ANDA eine progressiv kleinere Extinktion auf als der Ligand, abhängig von der Zunahme der HfO^{2+}-Ionenmenge.

(*2*) Bei 216,5 nm ist die Extinktion des Systems Hf-ANDA konstant und gleich der des Liganden. Hier steigt die Extinktion des Systems Zr-ANDA proportional mit der Zunahme der anwesenden ZrO^{2+}-Ionenmenge.

(*3*) In analoger Weise könnte man bei 243,5 nm (isosbestischer Punkt für das System

Zr-ANDA) Hf in Gegenwart von Zr und bei 242,5 nm (isosbestischer Punkt für das System Hf-ANDA)Zr in Gegenwart von Hf- bestimmen.
(*4*) Bei ungefähr 297 nm wird man die anwesende Zirkoniummenge und bei ungefähr 298 nm die Hafniummenge bestimmen können.

Für solche Bestimmungen kann man zwei Wege einschlagen, welche anschließend beschrieben werden.

Absorptionskurvenverfahren

Hier gibt es zwei Varianten: Wasser als Bezugsflüssigkeit bzw. Blindprobe als Bezugsflüssigkeit.

Wasser als Bezugsflüssigkeit. In diesem Fall sind die experimentellen Bestimmungen analog denen aus Abb. 1. Für jeden einzelnen isosbestischen Punkt müssen jedoch die Arbeitsbedingungen so gewählt werden, daß sie zu optimalen Werten der Extinktion führen.

Als Beispiel ist in Abb. 1 Diagramm A das Gebiet um den isosbestischen Punkt von 218 nm für den Zr-ANDA-Komplex und im Diagramm B das Gebiet um den isosbestischen Punkt von 297 nm für den Hf-ANDA-Komplex dargestellt. Den isosbestischen Punkten von 243,5 nm (für das System Zr-ANDA) und 242,5 nm (für das System Hf-ANDA) entsprechen die Diagramme A beziehungsweise B aus der Abb. 1 (in Citat 1).

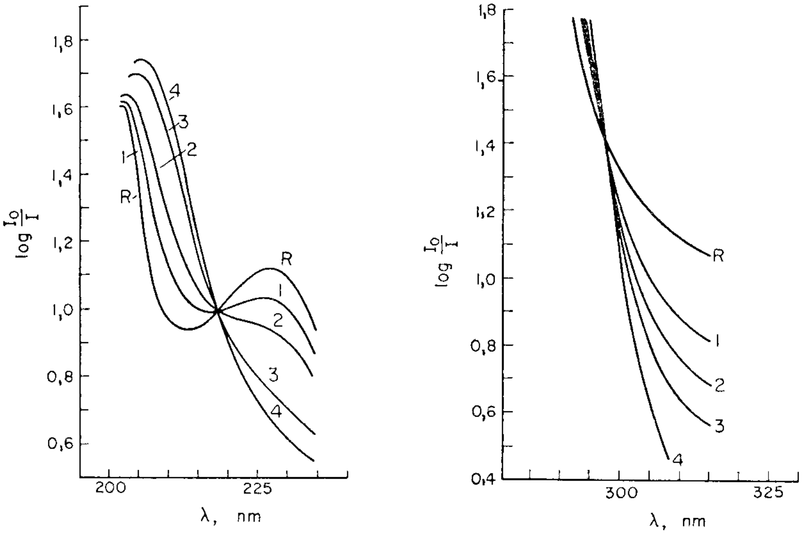
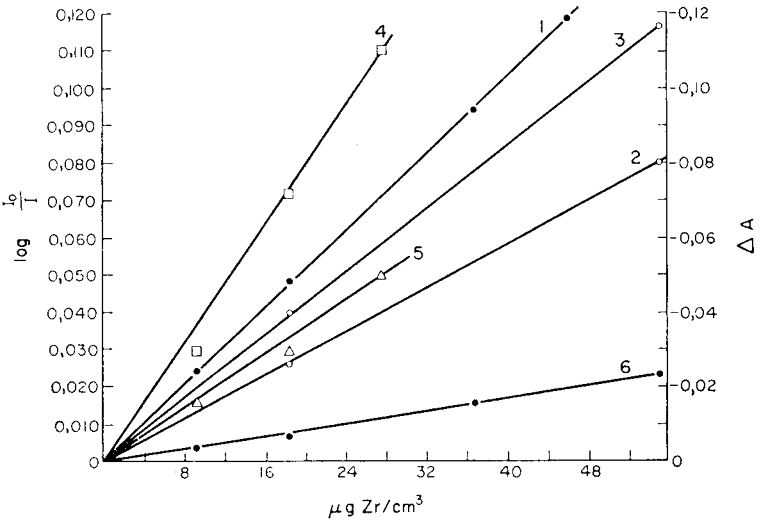


Abb. 1.—Absorptionskurven der Komplexe.
A: Zr-ANDA-Konstante Ligandkonzentration: 1,2 . 10^{-3}*M*. ZrO^{2+}-Konzentration: 0 (Kurve *R*), 10^{-4}*M* (Kurve *1*), 2 . 10^{-4}*M*. (*2*), 4 . 10^{-4}*M* (*3*), 5 . 10^{-4}*M* (*4*). Schichtdicke: 1 mm. *B*: Hf-ANDA. Konstante Ligandkonzentration: 1,6 . 10^{-3}*M*. HfO^{2+}-Konzentration: 0 (Kurve *R*), 2 . 10^{-4}*M* (Kurve *1*), 3 . 10^{-4}*M* (*2*), 4 . 10^{-4} (*3*), 6 . 10^{-4} (*4*). Schichtdicke: 20 mm. Bezugslösung für A und B = bidestilliertes Wasser.

Der Extinktionswert bei den entsprechenden Wellenlängen wird aus der graphischen Darstellung ermittelt. Abgelesen wird die Differenz zwischen der Extinktion der zu analysierenden Probe und der Eichprobe (Kurve *R*). Für eine genauere Ablesung der Extinktion wurde ein Epidiaskop oder eine Handlupe verwendet.



2A

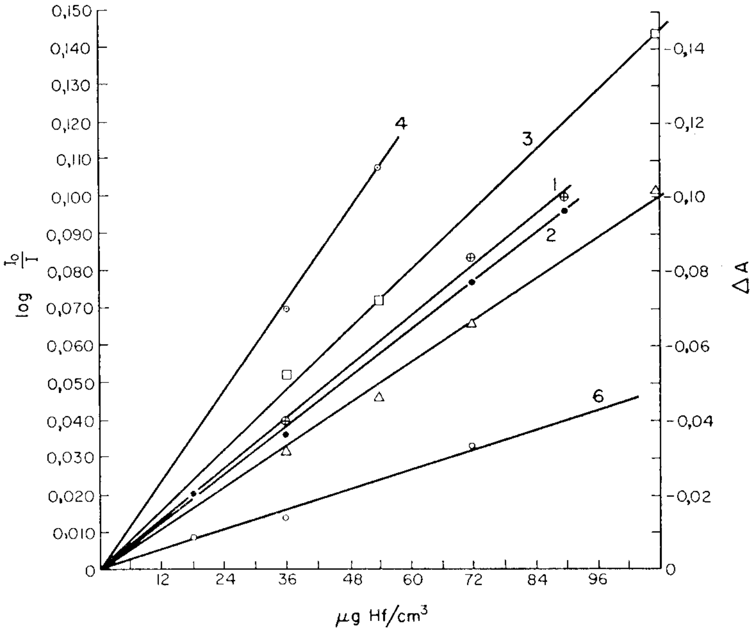
Abb. 2.—Eichkurven der Systeme.
Zr-ANDA (Diagramm A)

Kurve Nr.	Bezug	*nm*	Ligand-konzentration, *mM*	Schichtdicke, *mm*
1	bidest. Wasser	216,5	1,2	1
2	bidest. Wasser	242,5	1,6	2
3	bidest. Wasser	297	1,6	20
4	Blindlösung	215,5	1,2	2
5	Blindlösung	242,5	1,2	2
6	bidest. Wasser	297	2,6	5

Auf diese Weise (Abb. 2) werden die Eichkurven für den Komplex Zr-ANDA (Diagramm A) in den drei isosbestischen Punkten des Systems Hf-ANDA: 216,5 nm (Kurve *1*), 242,5 nm (Kurve *2*) und 297 nm (Kurve *3*) und auch die Eichkurven für den Komplex Hf-ANDA (Diagramm B) in den drei isosbestischen Punkten des Systems Zr-ANDA: 218,5 nm (Kurve *1*), 243 nm (Kurve *2*) und 298 5 nm (Kurve *3*) aufgestellt.

Die Absorptionskurven der Gemische (Zr + Hf)-ANDA haben dieselbe Form wie die Kurven *1–4* aus Abb. 3. Auch in diesem Fall werden für jedes Gebiet um die Wellenlänge des isosbestischen Punktes die Bedingungen so festgelegt, daß man optimale Werte für die Extinktionen erhält. Die aus einem Diagramm bei $\lambda = 216{,}5$ nm abgelesene Extinktion bezogen auf die Eichkurve (*R*) entspricht dem Komplex Zr-ANDA und die bei $\lambda = 218$ nm dem Komplex Hf-ANDA.

Ebenso entsprechen auch die abgelesenen Extinktionen aus einem analogen Diagramm wie Abb. 3 bei $\lambda = 242{,}5$ nm dem Komplex Zr-ANDA und bei $\lambda = 243{,}5$ nm dem Komplex Hf-ANDA. Für das Gebiet größerer Wellenlänge ($\lambda = 297$ nm, 298 nm) wird jede einzelne Kurve des Gemisches Zr + Hf aufgestellt, bei 297 für den Komplex Zr-ANDA, bei 298,5 nm, für den Komplex Hf-ANDA. Diese Messungen sind in Tabelle I für Zirkonium und in Tabelle II für Hafnium wiedergegeben. Aus den



2B

Hf-ANDA (Diagramm B)

Kurve Nr.	Bezug	*nm*	Ligand-konzentration, *mM*	Schichtdicke, *mm*
1	bidest. Wasser	218,2	1,2	1
2	bidest. Wasser	243,5	1,2	2
3	bidest. Wasser	298,5	1,6	20
4	Blindlösung	217,5	1,2	2
5	Blindlösung	243,5	1,6	2
6	bidest. Wasser	243	2,0	1,03

Kurven *1*, *3*, *4* und *6* (Diagramm A) und Kurven *2*, *5* und *6* (Diagramm B): Ordinate log I_0/I. Bie den anderen ist ΔA als Ordinate aufgetragen.

ersten 7 Spalten, die sich auf die oben beschriebenen Methoden beziehen, folgt, daß der prozentuale Fehler im Durchschnitt nicht 3% überschreitet.

Eine andere Möglichkeit Zirkonium in Gegenwart von Hafnium, aber nicht umgekehrt, zu bestimmen, entspringt aus einer besonderen Lage der Absorptionskurven beider Systeme im Wellenlängengebiet von 272–276 nm. Werden die Bedingungen so festgelegt, daß die Extinktion einen optimalen Wert aufweist, so erhält man die Diagramme aus Abb. 4, A für den Komplex Zr-ANDA, B für den Komplex Hf-ANDA und C für das Gemisch (Zr + Hf).

Bei 272–276 nm weist der Komplex Hf-ANDA eine konstante Extinktion auf. Sie ist gleich der des Liganden (Kurve *R*) und unabhängig von der anwesenden HfO^{2+}-Menge. Der Komplex Zr-ANDA zeigt eine Extinktion, die proportional mit der ZrO^{2+}-Menge in dem Reaktionsmedium wächst. Die Eichkurve für den Komplex Zr-ANDA bei $\lambda = 272{,}5$ nm ermöglicht die Bestimmung des Zirkonium (Tabelle I, Spalte B). Der durchschnittliche prozentuale Fehler beträgt ungefähr 4%.

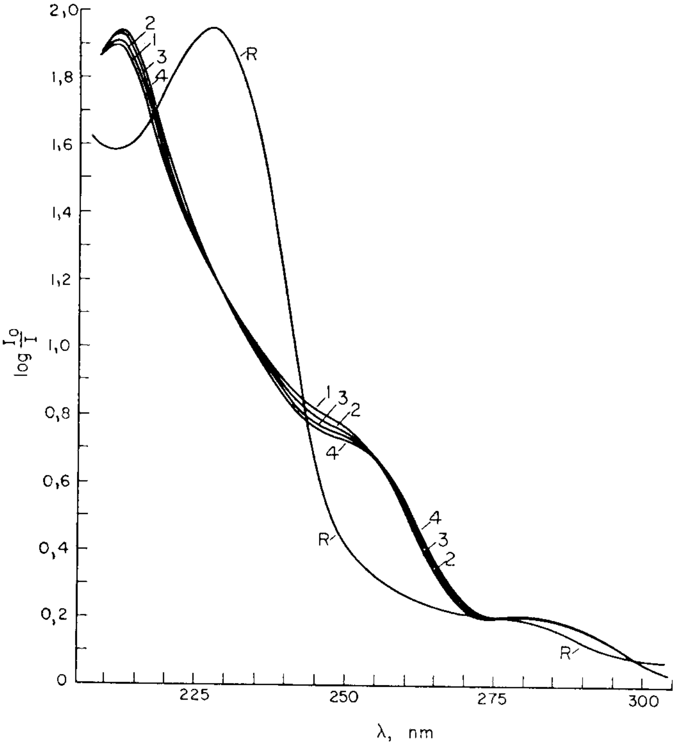


Abb. 3.—Absorptionskurven des Systems (Zr + Hf)-ANDA. Konstante ANDA-Konzentration: 1,2 . $10^{-3}M$. ZrO^{2+}-Konzentration: 0 (Kurve *R*), 1 . $10^{-4}M$ (Kurve *1*), 2 . $10^{-4}M$ (*2*), 3 . $10^{-4}M$(*3*), 4 . $10^{-4}M$ (*4*). HfO^{2+}-Konzentration: 0 (Kurve *R*), 4 . $10^{-4}M$ (Kurve *1*), 3 . $10^{-4}M$ (*2*), 2 . $10^{-4}M$ (*3*), 1 . $10^{-4}M$ (*4*). Bezugslösung: bidestilliertes Wasser. Schichtdicke: 2 mm.

Blindprobe als Bezugsflüssigkeit. Mit denselben Probelösungen, die zur Aufstellung der Diagramme aus Abb. 1 dienten, werden Absorptionskurven aufgenommen. Hier wird jedoch als Bezugsflüssigkeit eine Blindprobe verwendet (Kurve *R* aus Abb. 1). Man erhält so die Diagramme aus Abb. 5, A für den Komplex Zr-ANDA und B für Hf-ANDA. Auf diese Weise wird die Extinktion des Liganden kompensiert. Die Schnittpunkte der Kurven untereinander und mit der Nullinie stellen die isosbestischen Punkte in der neuen graphischen Darstellung dar. Da die Prinzipien dieselben sind, ist auch die Arbeitsweise analog mit der aus dem Verfahren 1.

Bei der Wellenlänge des isosbestischen Punktes des Komplexes Zr-ANDA wird die Extinktion für den Komplex Hf-ANDA abgelesen und umgekehrt. Bei 215,2 nm und bei 242,5 nm wurden die Eichkurven *4* und *5* aus Abb. 2, A für Zr-ANDA aufgestellt. Die in Tabelle I, Spalte 10–13 wiedergegebenen Werte zeigen, daß der prozentuale Fehler 3% nicht überschreitet. Für den Komplex Hf-ANDA wurden die Eichkurven *4* und *5* aus Abb. 2B bei λ = 217,5 nm bzw. bei 243,5 nm aufgestellt. Die in Tabelle II Spalte 8–11 wiedergegebenen Werte zeigen, daß bei den angegebenen Mengenverhältnissen der durchschnittliche prozentuale Fehler 3% beträgt. Der isosbestische Punkt von 297–298 nm kann bei diesem Verfahren nicht ausgewertet werden, weil die Extinktionsdifferenzen zu klein sind. Die Anwendung einer Skalenausdehnung würde wahrscheinlich auch hier eine Bestimmung ermöglichen. Infolge

TABELLE I.—SPEKTROPHOTOMETRISCHE BESTIMMUNG DES ZIRKONIUMS IN GEGENWART VON HAFNIUM

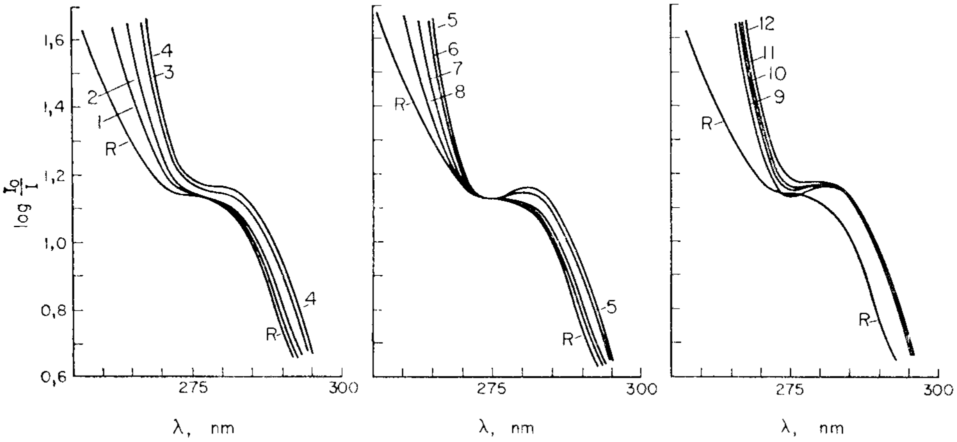
Zr gegeben *μg/ml*	Zr gefunden,* *μg/ml*								Zr gefunden,† *μg/ml*				Zr gefunden,‡ *μg/ml*	
	λ = 216,5 *nm*	Δ	λ = 242,5 *nm*	Δ	λ = 297 *nm*	Δ	Gebiet λ = 272,5 *nm*	Δ	λ = 215,2 *nm*	Δ	λ = 242,5 *nm*	Δ	λ = 297 *nm*	Δ
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1,8$_2$	—	—	—	—	—	—	—	—	—	—	—	—	1,8	—
3,6$_4$	—	—	—	—	—	—	3,8	+0,2	—	—	—	—	—	—
9,1$_2$	8,8	−0,3	—	—	—	—	9,7	+0,5	9,3	+0,2	9,1	0	9,1	0
14,6	—	—	—	—	—	—	15,0	+0,4	—	—	—	—	—	—
18,2	18,2	0	17,9	−0,3	18,6	+0,4	—	—	18,2	0	17,7	−0,5	17,5	−0,7
27,4	26,6	−0,7	27,7	+0,3	26,6	−0,7	—	—	27,4	0	27,4	0	—	—
36,5	36,5	0	37,6	+1,1	35,9	−0,5	—	—	—	—	—	—	—	—

* Das Absortionskurvenverfahren mit Wasser als Bezugsflüssigkeit.
† Das Absortionskurvenverfahren mit Blindprobe als Bezugsflüssigkeit.
‡ Das Meßverfahren bei konstanter Wellenlänge.

TABELLE II.—SPEKTROPHOTOMETRISCHE BESTIMMUNG DES HAFNIUMS IN GEGENWART VON ZIRKONIUM

Hf gegeben, *μg/ml*	Hf gefunden,* *μg/ml*						Hf gefunden,† *μg/ml*				Hf gefunden,‡ *μg/ml*	
	λ = 218,2 *nm*	Δ	λ = 243,5 *nm*	Δ	λ = 298,5 *nm*	Δ	λ = 217,5 *nm*	Δ	λ = 243,5 *nm*	Δ	λ = 243 *nm*	Δ
1	2	3	4	5	6	7	8	9	10	11	12	13
3,5$_6$	—	—	—	—	—	—	—	—	—	—	3,3$_9$	−0,1$_7$
7,1$_3$	—	—	—	—	—	—	—	—	—	—	7,1$_3$	0
17,8	17,8	0	17,8	0	—	—	17,8	0	—	—	—	—
35,7	34,3	−1,4	35,7	0	34,3	−1,4	35,0	−0,7	35,0	−0,7	34,6	−1,1
53,5	52,1	−1,4	52,8	−0,7	53,5	0	53,5	0	51,8	−1,8	—	—
71,4	72,1	+0,7	70,7	−0,7	71,4	0	—	—	71,4	0	—	—

* Das Absortionskurvenverfahren mit Wasser als Bezugsflüssigkeit.
† Das Absortionskurvenverfahren mit Blindprobe als Bezugsflüssigkeit.
‡ Das Meßverfahren bei konstanter Wellenlänge.



(A) (B) (C)

ABB. 4.—Absorptionskurven der Systeme: Zr-ANDA (Diagramm A), Hf-ANDA (Diagramm B) und (Zr + Hf)-ANDA (Diagramm C). Konstante Ligandkonzentration = $1{,}2 \cdot 10^{-3}M$. ZrO^{2+}-Konzentration: 0 (Kurve *R*), $1 \cdot 10^{-4}M$ (Kurve *1*), $2 \cdot 10^{-4}M$ (*2*), $4 \cdot 10^{-4}M$ (*3*), $5 \cdot 10^{-4}M$ (*4*). HfO^{2+}-Konzentration: 0 (Kurve *R*), $5 \cdot 10^{-4}M$ (Kurve *5*), $4 \cdot 10^{-4}M$ (*6*), $2 \cdot 10^{-4}M$ (*7*), $1 \cdot 10^{-4}M$ (*8*). Den Kurven *9*, *10*, *11*, *12* und *1*, *2*, *3*, *4* liegt die gleiche ZrO^{2+}-Konzentration zu Grunde. Die HfO^{2+}-Konzentration entspricht der der Kurven *5*, *6*, *7* und *8*. Bezugslösung: bidestilliertes Wasser. Schichtdicke: 10 mm.

der hohen Extinktion der Lösung in der Bezugsküvette und infolge des kleinen molaren Extinktionskoeffizienten der Systeme Zr– Hf–ANDA sind keine größeren Absorptionswerte zu erzielen. Aus denselben Gründen ist auch die Aufstellung der Kurven im Gebiet kleinerer Wellenlängen als 225 nm an größere Feher gebunden.

Meßverfahren bei konstantem λ

Die gleichzeitige Bestimmung von Zirkonium und Hafnium kann auch nur mit Hilfe eines nichtautomatischen Spektrophotometers durchgeführt werden. In diesem Falle sind aber nur Bestimmungen möglich, bei denen der Extinktionswert positiv ist. So kann man bei ungefähr 243 nm Hafnium bestimmen. Bei 297 nm kann man dagegen Zirkonium in Gegenwart von Hafnium erfassen, da sich die Absorptionskurven der Komplexe Zr-ANDA im Intervall zwischen diesen beiden Wellenlängen scheiden. Die Bestimmung des Zirkonium bei ungefähr 216 nm ist hier nicht möglich, weil die Messungen bei kleineren Wellenlängen als 220 nm zu ungenau sind.

Für die möglichen, obenangeführten Bestimmungen, zum Beispiel die Hf-Bestimmungen bei ungefähr 243 nm, wird wie folgt verfahren. Die Extinktion der Blindlösung (die alles, außer der Kationenlösung enthält) wird (bezogen auf Wasser) im Intervall von einigen nm um den, für den Komplex Zr-ANDA bekannten isosbestischen Punkt (aus Abb. 1), ermittelt. Für 2 bis 3 Proben, die den Komplex Zr-ANDA mit veränderlichen Zr-Mengen enthalten, wird die Extinktion bei denselben Wellenlängen gemessen. Ausgesucht wird die Wellenlänge, bei der die Extinktion aller Proben identisch und gleich der der Blindprobe ist. Bei dieser Wellenlänge nimmt man die Extinktion einer Eichserie für den Komplex Hf-ANDA (Kurve *6* aus Abb. 3B)

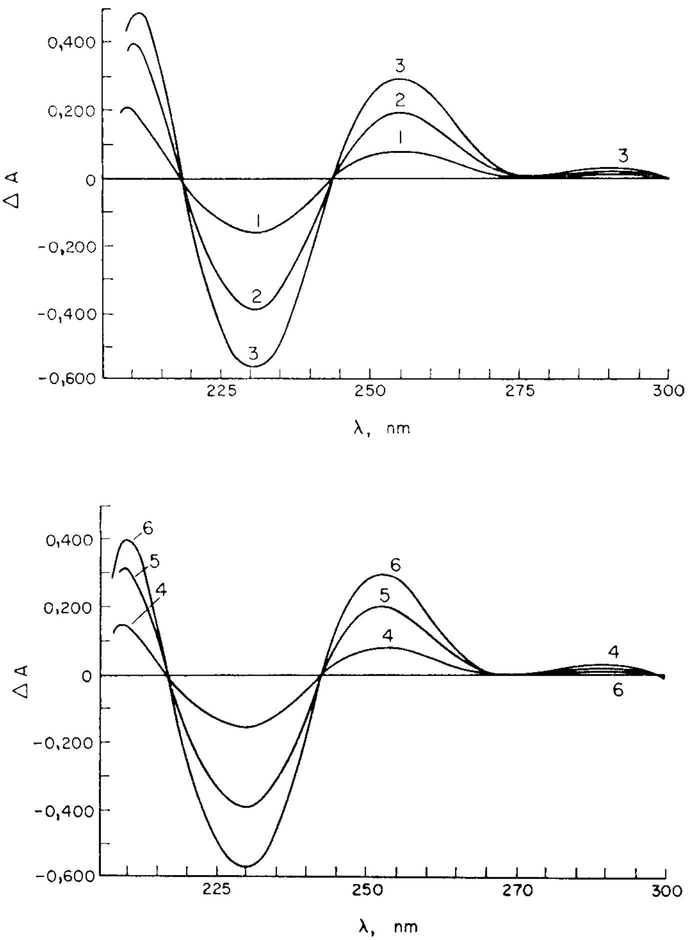


Abb. 5.—Absorptionskurven der Komplexe Zr-ANDA (Diagramm A) und Hf-ANDA (Diagramm B).
Konstante Ligandkonzentration = $0{,}4 \cdot 10^{-3}M$. ZrO^{2+}-Konzentration: $0{,}4 \cdot 10^{-4}M$ (Kurve *1*), $1 \cdot 10^{-4}M$ (*2*), $1{,}6 \cdot 10^{-4}M$ (*3*). HfO^{2+}-Konzentration: $0{,}4 \cdot 10^{-4}M$ (Kurve *4*), $1 \cdot 10^{-4}M$ (*5*), und $1{,}6 \cdot 10^{-4}M$ (*6*). Bezugslösung: Blindlösung. Schichtdicke 5 mm.

auf. Die anschließend gemessene Extinktion für ein Gemisch (Zr + Hf)-ANDA kann ausschließlich dem Komplex Hf-ANDA zugeschrieben werden. In Tabelle II zeigen die Spalten 12 und 13, daß bei Lösungen, in welchen ~2,5 % Hafnium im Vergleich zu Zirkonium enthalten sind, ein prozentualer Fehler von ~5 % auftritt. Für größere Zr-Gehalte liegt dieser aber bei $\leq 3\%$. Im Falle der Zr-Bestimmung bei der Wellenlänge von ungefähr 297 nm verfährt man analog. Erhalten wird so die Eichkurve *6* aus Abb. 3A. Beispiele für solche Bestimmungen sind in Tabelle I, Spalte 14, angegeben. Auch hier besteht die Möglichkeit gegen die Blindprobenlösung zu photometrieren. In diesem Fall kann die Extinktion aus den Eichdiagrammen (erhalten durch Differenzbildung: Extinktion der Versuchsprobe minus Extinktion der Blindprobe, beide bezogen auf Wasser) direkt abgelesen werden. Größere

Fehler, die bei der Messung sehr kleiner Extinktionen auftreten, machen das erste Verfahren vorteilhafter.

Im folgenden wird die spektrophotometrische Bestimmung des Zirkoniums und Hafniums bei den Wellenlängen $\lambda \sim 216$ bzw. 218 nm kurz beschrieben.

Zur Aufstellung der Eichkurven für das ZrO^{2+}-Ions werden vier Proben mit je 3 ml $10^{-4}M$ ANDA und 0,5–2,5 ml $5 . 10^{-3}N$ $ZrOCl_2$, gelöst in $10^{-1}M$ Perchlorsäure eingesetzt. Diese vier Kurven nebst der der Bezugsprobe *R* (Lösung sämtlicher Komponenten außer $ZrOCl_2$) bilden Diagramm A. Verfährt man analog für das Ion HfO^{2+}, so erhält man Diagramm B.

Aus Diagramm A wird bei $\lambda = 216{,}5$ nm die Differenz der Absorptionen zwischen jeder der Absorptionskurven und der Kurve *R* abgelesen und mit diesen Werten die Eichkurve der ZrO^{2+}-Ions aufgestellt. Aus Diagramm B wird bei $\lambda = 218$ nm analog die Eichkurve für HfO^{2+} erhalten.

Schließlich wird die Absorptionskurve einer Lösung, welche dieselbe Ligandmenge (3 ml $10^{-2}M$ ANDA und ein Gemisch von ZrO^{2+} und HfO^{2+}) enthält, aufgenommen. Die Summe von Zirkonium und Hafnium darf jedoch $1{,}25 . 10^{-5}$ Mol nicht überschreiten. In Diagramm C ist diese Absorptionskurve mit Bezugskurve *R* enthalten. Die Differenz beider Extinktionen bei der Wellenlänge $\lambda = 216{,}5$ nm entspricht dem Komplex Zr-ANDA. Die Konzentration des ZrO^{2+} hingegen wird aus der Eichkurve des Systems A entnommen. Die Extinktion bei der Wellenlänge $\lambda = 218$ nm entspricht dem Hf-ANDA-Komplex, die Konzentration des HfO^{2+} läßt sich dann aus der Eichkurve des Systems B ermitteln.

Summary—Zirconium may be determined in the presence of hafnium by ultraviolet spectrophotometry at the isosbestic wavelengths of 218·2, 243·3 or 298·8 nm, with anthranil-*N*,*N*,-diacetic acid in dilute acid solution. Hafnium may be determined in the presence of zirconium from measurements at 216·5, 242·5 or 297 nm. Concentrations in the range 2–36 μg/ml (Zr) and 3–70 μg/ml (Hf) may be determined, and in admixture, from 2·5 to 80% of Zr in Hf, and *vice versa*, with an error of 3–4%.

Résumé—On peut déterminer le zirconium en la présence de hafnium par spectrophotométrie ultra-violette aux longueurs d'ondes isosbestiques de 218,2, 243,5 ou 298,5 nm, avec l'acide anthranil *N*,*N*-diacétique en solution d'acide dilué. On peut déterminer le hafnium en la présence de zirconium des mesures à 216,5; 242,5 ou 297 nm. On peut déterminer des concentrations dans les domaines 2–36 μg/ml (Zr) et 3–70 μg/ml (Hf), et en mélange, de 2,5 à 80% de Zr dans Hf, et vice versa, avec une erreur de 3–4%.

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ANALYSIS BY PHASE TITRATION OF THREE-COMPONENT SYSTEMS CONTAINING TWO MUTUALLY IMMISCIBLE COMPONENTS

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Summary—A method, based on phase titration, for the analysis of ternary mixtures containing two mutually immiscible or partially miscible components is described. It can also be used for the determination of tie-lines. The method is illustrated by its application to the system consisting of benzene, cyclohexane and nitromethane.

THE PRINCIPLE of phase titrations has been used for many years to analyse binary solutions of components which are chemically similar but have different solubilities in water, by titrating the sample with water.[1] If the amount of water that was added is known, the composition of the binary system can be computed from the phase diagram. Siggia and Hanna[2] extended the technique to compute the composition of one-phase ternary systems containing two mutually immiscible components. In their method, one of the components was estimated by chemical or physical means. A separate sample was then titrated with one of the mutually immiscible components, until a turbidity appeared. The composition of the sample was then computed from the ternary phase diagram. More recently Rogers and co-workers[3] have done extensive work on phase titrations and have discussed the titration behaviour of ternary systems, on the basis of solubility relationships.

In the present communication, a method based on the principle of phase separation titration is described, which can be used to analyse a ternary mixture containing two mutually immiscible or partially miscible components, without separate determination of any component. The method can also be used to determine the tie-lines in such ternary systems and has several advantages over other methods. The time for the total analysis is considerably shortened and the errors involved in chemical determination of the components are avoided. The method can be used for systems where chemical analysis for any of its components is difficult.

Technique

The ternary phase diagram is first determined. This can be done easily by phase separation titration.[4] In order to get sharp turbidimetric end-points and to improve the accuracy of the determination, various solutions of the mutual solvent with each of the mutually immiscible components, richer in the latter, are prepared by weight and titrated with the other mutually immiscible component until a permanent turbidity appears. Such turbidimetric end-points can usually be obtained within a drop of titrant.[2]* The ternary mixture is then weighed to determine the weight of the

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* Dunnery and Atwood[5] preferred the clarification end-point to the turbidimetric end-point, the former being equally sharp over a wide composition range. The visibility of the end-point can be improved by the addition of colour contrast indicators, *e.g.*, iodine[6] and furfural.[7]

titrant added. The concentrations of the two sets of binary solutions are chosen so as to yield some overlapping points in the middle region of the curve on titration with the third component. This serves as an internal check on the determination and also illustrates the reproducibility of the technique.[8]

Consider a three-component system containing *A*, *B* and *C*, where *A* and *B* are mutually immiscible and *C* is miscible with both *A* and *B*. If to 1 g of the ternary solution having the composition represented by any point, **P**, on the binodal curve (Fig. 1), 1 ml (it is more practicable to add a known volume than a known weight) of component *C* is added, the composition of the resultant solution can now be represented by **Q**, a point on the line connecting **P**, representing the original composition and **C**, representing 100% *C*. On titration with *B*, the composition of this solution will move along the line **QB** and a permanent turbidity will appear when the composition reaches **R**, the point of intersection of the line **QB** with the binodal curve. The weight of component *B* required to produce permanent turbidity* thus depends upon the composition of the solution represented by **P** and **R** and is given by the expression:

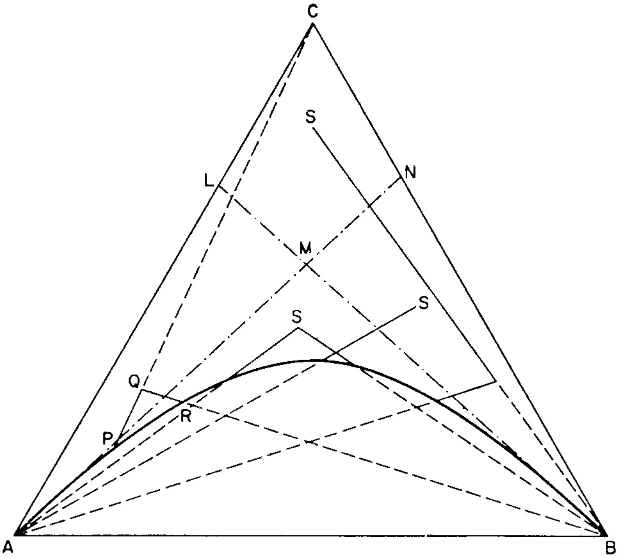

FIG. 1.—Ternary liquid-liquid miscibility diagram illustrating the analysis of the ternary mixture, S, by phase titrations.

$$W_B = \frac{X_{AP}}{X_{AR}} - (1 + W_C)$$

where W_C is the weight of component *C* added per g of the solution with composition **P**; W_B is the weight of titrant *B* required to titrate $(1 + W_C)$ g of solution from **Q** to **R**, *i.e.*, to the turbidimetric end-point, and X_{AP} and X_{AR} are the weight fractions of component *A* at compositions **P** and **R** respectively.

Once the binodal curve is determined, the amount of *A* or *B* required to produce a

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* Which non-con-solute component is selected as titrant depends upon the composition of the ternary to be titrated.[2]

turbidimetric end-point for a mixture of 1 g of a ternary composition lying on the binodal curve, and 1 ml of component *C*, for various amounts of *A* initially present can be calculated. Two calibration curves can then be plotted indicating the amount of *A* or *B* required to titrate such solutions, as a function of the amount of *A* or *B* in the initial ternary solution at **P**.

On addition of 1 ml of the component *C* to 1 g of a ternary composition lying on the binodal curve, if the composition of the resultant mixture lies outside **ALMNB,** the area defined by the tangents to the binodal curve, it will not yield any turbidimetric end-point on titration with either *A* or *B*. In such cases, for plotting the calibration curves the sample solution and component *C* are mixed in some other simple ratio such as 2 g/ml, 3 g/ml instead of 1 g/ml, and the amount of component *C* required to produce turbidity is calculated.

Determination of tie-lines

The composition of any ternary mixture lying on the binodal curve can be determined by adding 1 ml of *C* per g of the ternary mixture and titrating with *A* or *B*. From the amount required, the initial composition of the ternary can be computed from the calibration curves.

In order to determine the tie-lines, the composition of both the phases in equilibrium is computed as described above by running two sets of titrations for each phase, one with *A* and the other with *B*.

Analysis of ternary mixtures

To analyse a homogeneous mixture of *A*, *B* and *C*, having a composition represented by any point, **S**, other than on the binodal curve, two samples of known weight of the ternary are titrated with each of components *A* and *B* to bring the composition of the ternary on to the binodal curve. The solution is then weighed and the weight of *A* or *B* added is determined. The composition of this solution is then obtained as described above and hence the initial composition of the ternary is calculated.

If the composition of the ternary mixture lies somewhere in the area **CLMN**, a known weight of *A* or *B* is added to a known weight of the ternary, enough to bring the composition into either of the titratable regions **BNM** or **ANL**. The solution thus obtained is titrated with the other mutually immiscible component to the turbidimetric end-point and hence the composition of the ternary is determined. The amount of *A* or *B* sufficient to bring the composition of unit weight of the ternary into the titratable region can be calculated from the position of **L** and **N** (Fig. 1).

The method described is illustrated for the ternary system benzene, cyclohexane and nitromethane, the last two being partially miscible at ordinary temperatures.

EXPERIMENTAL

Procedure

The solvents were purified by established methods.[9,10] Their densities measured at 30° and 40° (±0·01°) are given in Table I, along with the literature values for comparison.[11]

The binodal curve was established at 40° as described earlier.[8] The technique and apparatus used were similar to those of Dunnery and Atwood.[5] The solutions and the solvents were kept in a thermostatic cabin before use, the temperature of the cabin during titrations being kept constant to within 0·1°. Enough solution was taken to give a titre of 10–20 ml. The results obtained are tabulated in Table II and are in good agreement with those obtained by Weck and Hunt[12] at 25° and by Suri *et al.*[8] at 20° and 30°.

TABLE I.—DENSITIES OF THE SOLVENTS USED

	Temp., °C	Present work, g/ml	Literature[11] g/ml
Benzene	30	0·8685	0·8685
	40	0·8575	0·8577
Cyclohexane	30	0·7694	0·7692
	40	0·7596	0·7594*
Nitromethane	30	1·1250	1·1245
	40	1·1108	—

* Value at 40·21°C.

TABLE II.—COMPOSITION AT THE BINODAL CURVE FOR THE SYSTEM C_6H_6—C_6H_{12}—CH_3NO_2 AT 40°C

Cyclohexane, % w/w	Nitromethane, % w/w	Cyclohexane, % w/w	Nitromethane, % w/w
9·2	85·3	42·1	34·1
11·6	77·8	50·7	25·2
15·4	69·2	59·6	18·2
19·3	62·5	65·3	15·4
25·0	53·9	83·8	7·3
35·0	42·1	93·4	5·1

Since the addition of 1 ml of benzene to 1 g of the binodal curve ternary moved its composition outside the area **ALMNB** (Fig. 1) for most of the compositions, the two were mixed in the ratio 1 ml: 3 g for the system under study. The compositions of the resultant mixtures for various **P** values (Fig. 2) were calculated and are represented by **Q** values. The **Q** values were then joined with the apices corresponding to 100% cyclohexane and nitromethane, and from the composition of **R**, where one of these lines intersected the binodal curve, the amounts of cyclohexane or nitromethane required to produce a turbidimetric end-point were calculated. Two calibration curves were then drawn

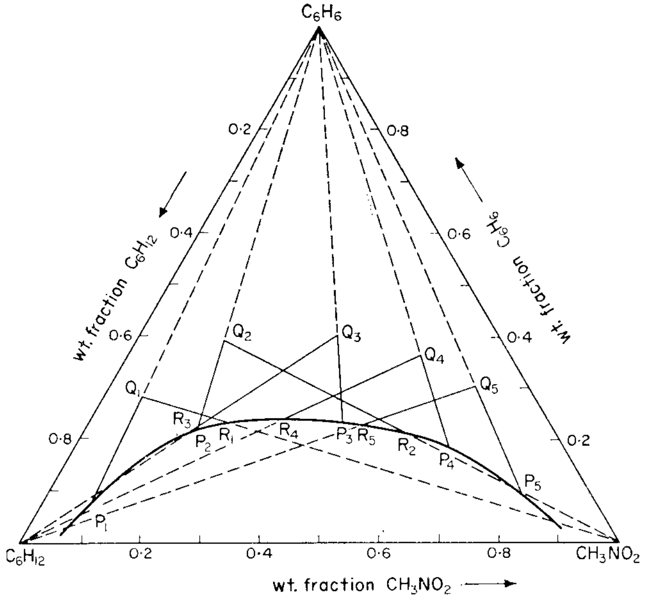

FIG. 2.—Determination of the amount of titrant required to construct the calibration curve for the ternary system benzene–cyclohexane–nitromethane at 40°C.

plotting the composition of the ternary at **P** *vs.* the amount of cyclohexane or nitromethane required to produce turbidity at the corresponding **Q**.

Results

Ten synthetic ternary mixtures were prepared by mixing different amounts of benzene, cyclohexane and nitromethane and were analysed by this method. The results obtained are compared with the actual values in Table III.

TABLE III.—COMPARISON OF THE ACTUAL AND THE ESTIMATED COMPOSITION OF THE TERNARY MIXTURE $C_6H_6 + C_6H_{12} + CH_3NO_2$

Sample	Cyclohexane, % *w/w*		Nitromethane, % *w/w*		Titrant
	Present	Estimated	Present	Estimated	
1	72·0	71·8	6·3	6·5	Nitromethane
2	50·8	49·9	12·2	12·4	Nitromethane
3	39·4	39·1	27·3	26·8	Cyclohexane
		39·6		26·4	Nitromethane
4	6·0	6·13	79·1	80·6	Cyclohexane
5	7·8	7·62	58·8	58·9	Cyclohexane
6	27·6	27·6	45·0	44·7	Cyclohexane
		28·2		45·8	Nitromethane
7	9·6	9·67	14·4	14·4	Cyclohexane
		10·1		14·8	Nitromethane
8	34·8	34·9	10·1	10·2	Cyclohexane
		35·3		10·4	Nitromethane
9	25·4	25·0	24·8	24·4	Cyclohexane
		25·2		25·7	Nitromethane
10	0·0	0·2	38·5	38·1	Cyclohexane
		0·1		38·3	Nitromethane

Samples 1 and 2 gave turbidimetric end-points with nitromethane, 4 and 5 with cyclohexane, 3 and 6 with both and 7–10 with neither. Two sets of each of samples 7–10 were diluted with about the same weight (because the position of **L** and **M** lies at ~0·5 weight-fraction) of nitromethane or cyclohexane and the resultant mixtures were titrated with cyclohexane or nitromethane respectively. The composition of the turbid solution obtained on titration with nitromethane or cyclohexane for all the samples was computed from the calibration curve by determining the amount of titrant required to titrate a mixture of 0·333 ml of benzene and 1 g of this solution to the turbidimetric end-point. The composition of the unknown ternary was then calculated.

DISCUSSION

It can be seen from Table III that the agreement between the actual and the determined values is satisfactory on the whole. The maximum difference is ~1·5% when cyclohexane is used and ~4% when nitromethane is used as titrant, indicating that the latter is a poor titrant for phase titrations. A similar observation was made earlier by Rogers and co-workers[13] for nitromethane. The agreement between the actual value and the two sets of determined values for samples 3, 6, and 7–10 is good.

Although the method described above is extremely useful when it is difficult to determine any of the components chemically, it is subject to certain limitations. If the refractive indices of the two phases produced are nearly the same, an opalescence instead of a turbidity will be observed near the end-point. The end-point will be invisible if the refractive indices are the same (iso-optic area). In such cases, addition of few drops of one of the three pure components to an aliquot of the sample is expected to help in locating the end-point. Various other sources of error are inadequate temperature control, evaporation losses during titration, errors involved in determining the phase diagram and lack of a sharp end-point in certain cases.

Zusammenfassung—Eine auf Phasentitration beruhende Methode zur Analyse ternärer Gemische wird beschrieben, die zwei nicht oder nur teilweise mischbare Komponenten enthalten. Sie kann auch zur Ermittlung von Konnoden dienen. Die Methode wird an ihrer Anwendung auf das System Benzol-Cyclohexan-Nitromethan erklärt.

Résumé—On décrit une méthode basée sur le titrage de phase pour l'analyse de mélanges ternaires contenant deux constituants mutuellement non miscibles ou partiellement miscibles. On peut aussi l'utiliser pour la détermination de lignes de jonction. La méthode est illustrée par son application au système consistant en benzène, cyclohexane et nitrométhane.

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DETERMINATION OF VANADIUM IN REFRACTORY METALS, STEEL, CAST IRON, ALLOYS AND SILICATES BY EXTRACTION OF AN NBPHA COMPLEX FROM A SULPHURIC–HYDROFLUORIC ACID MEDIUM

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Summary—A method for determining up to 0·15% of vanadium in high-purity niobium and tantalum metals, cast iron, steel, non-ferrous alloys and silicates is described. The proposed method is based on the extraction of a red vanadium(V)-*N*-benzoyl-*N*-phenylhydroxylamine complex into chloroform from a sulphuric–hydrofluoric acid medium containing excess of ammonium persulphate as oxidant. The molar absorptivity of the complex is 428 l.mole^{-1}.mm^{-1} at 475 nm, the wavelength of maximum absorption. Interference from chromium(VI) and cerium(IV) is eliminated by reduction with iron(II). Common ions, including large amounts of titanium, zirconium, molybdenum and tungsten, do not interfere.

NUMEROUS methods have been reported for the spectrophotometric determination of vanadium with *N*-benzoyl-*N*-phenylhydroxylamine (NBPHA).[1–12] In these methods, vanadium(V), as a purple 1:2 complex, is extracted into chloroform from a hydrochloric acid medium. Ryan[1] and Priyadarshini and Tandon[2] have stated that extraction of vanadium is quantitative under considerably different conditions of acid concentration, *i.e.*, from 5–9*M* and from 2·8–4·3*M* hydrochloric acid, respectively. However, other investigators[6,13] have found that extraction is not quantitative because of partial reduction of vanadium in relatively concentrated hydrochloric acid solutions. Because similar problems (low and erratic results), associated with the use of hydrochloric acid media, were encountered in this laboratory, an attempt was made to find a more suitable medium for extraction. Subsequently, it was established that the purple complex can be extracted readily from sulphuric acid (optimum concentration 3·0–3·5*M*)–sodium chloride (0·5–>2*M*) media containing excess of ammonium persulphate as oxidant, and that it has a higher molar absorptivity (498 l.mole^{-1}.mm^{-1} at 525 nm) than has been reported previously.[1–3]

In experiments testing the masking effect of fluoride on ions known to interfere with the extraction of the purple complex (*e.g.*, titanium, zirconium),[2,13,14] a change in colour of the extract to a reddish hue and a subsequent decrease in the wavelength of maximum absorption were observed. These changes were found to be more pronounced with increasing fluoride concentration and indicated the formation of a different complex in the presence of fluoride. Because of the beneficial complexing effect of fluoride, it was considered that a method based on extraction of the red vanadium complex from a fluoride medium would be more selective than one based on extraction of the purple complex from a chloride medium. Consequently, the conditions of formation and extraction of the red complex were investigated in the present work. The applicability of this extraction method to the determination of small amounts of vanadium in a variety of materials, including high-purity niobium and tantalum metals, is demonstrated.

EXPERIMENTAL

Apparatus

Funnels for filtering extract. Constructed from broken 10-ml pipettes by cutting the bulb in half.

Reagents

Standard vanadium solution. Dissolve 0·1785 g of vanadium pentoxide by heating in a 250-ml beaker with 40 ml of 12·5*M* sulphuric acid and 5 ml of concentrated nitric acid. Evaporate the resulting solution to fumes of sulphur trioxide, cool, and dilute to 500 ml with water. Prepare a working solution (1 ml ≡ 25 μg of vanadium) by appropriate dilution of this stock solution. (The vanadium pentoxide used was found to be pure by reduction and titration with permanganate.)

NBPHA solution. Prepare a 0·1% w/v solution-in chloroform and store in a brown bottle.

Iron(II) ammonium sulphate hexahydrate, 10% *solution, w/v.* Dissolve 5 g of the reagent in water, add 1 ml of 12·5*M* sulphuric acid and dilute to 50 ml with water. Prepare fresh as required.

Ammonium persulphate, 10% *solution, w/v.* Prepare fresh as required.

Sulphuric acid, 12·5*M.*

Hydrofluoric acid, 25*M.*

Chloroform (alcohol-free).[2]

Calibration curve

Add 8 ml of 12·5*M* sulphuric acid to each of seven 125-ml polypropylene separatory funnels (marked at 50 ml); then by burette, add to the last six funnels 1, 2, 3, 4, 5 and 6 ml, respectively, of standard 25 μg/ml vanadium solution. The first funnel contains the blank. Add to each funnel 8 ml of 25*M* hydrofluoric acid, 4 ml of 10% iron(II) ammonium sulphate solution, dilute to approximately 40 ml with water and mix. Then add 5 ml of 10% ammonium persulphate solution, dilute to the 50-ml mark with water and mix thoroughly. Add 10 ml of 0·1% NBPHA chloroform solution, stopper and shake for 2 min. Allow several min for the layers to separate, then filter the chloroform extract through a wad of cotton-wool into a dry 25-ml volumetric flask. Re-extract the solution three more times using, in succession, 5, 3 and 3 ml of NBPHA solution and shaking for 2 min each time. Combine these extracts with the first, wash the funnel with a few ml of chloroform and dilute to volume with chloroform. Determine the absorbance of each solution against chloroform as the reference solution, using 20-mm cells, at a wavelength of 475 nm. Correct the absorbance value obtained for each vanadium-NBPHA extract by subtracting that obtained for the blank. Plot μg of vanadium *vs.* absorbance.

Procedures

In the following procedures a reagent blank is carried along with the samples.

Niobium and tantalum metals. Transfer a suitable weight (0·1–0·5 g) of the powdered metal to a 250-ml Teflon beaker, add 5 ml of water, 8 ml of 12·5*M* sulphuric acid solution and 2 ml of hydrofluoric acid and cover the beaker with a Teflon cover. Add 4 ml of concentrated nitric acid, heat gently until all of the metal is in solution, then remove the cover and evaporate the solution to fumes of sulphur trioxide. After cooling, wash down the sides of the beaker with a small amount of water, add 1 ml of hydrofluoric acid and again evaporate to fumes to ensure complete removal of nitric acid. Cool, add 5 ml of water, allow to cool to room temperature and then, just before the extraction step, add 8 ml of 25*M* hydrofluoric acid solution (hydrofluoric acid volatilizes from the solution on prolonged standing at room temperature). Swirl the beaker to dissolve precipitated hydrates of niobium or tantalum, transfer the resulting solution to a 125-ml polypropylene separatory funnel and, after the addition of iron(II) ammonium sulphate and ammonium persulphate solutions, proceed with the extraction and determination of vanadium as described above.

Silicate rocks. Decompose a suitable weight of sample (0·1–0·5 g) depending on the expected vanadium content, by the method described for niobium and tantalum metals, using 5 ml of hydrofluoric acid instead of 2 ml (additional hydrofluoric and nitric acids may be required to obtain complete dissolution). After evaporating the resulting solution twice to fumes of sulphur trioxide, cool, add 5 ml of water and heat gently (if necessary) to clarify the solution. Add 8 ml of 25*M* hydrofluoric acid solution (calcium, in large amounts, is insoluble in this acid mixture but this does not impair the extraction of vanadium), transfer the resulting solution to a separatory funnel and proceed with the extraction and subsequent determination of vanadium.

Steel, cast iron and non-ferrous alloys (low chromium content). Decompose a 0·1–0·5-g sample containing not more than approximately 10 mg of chromium, by the method described for niobium and tantalum metals and determine vanadium as described above. With samples of cast iron, remove graphitic carbon before the extraction step, by filtering (plastic funnel) the resulting sulphuric–hydrofluoric acid solution into the separatory funnel.

Steel and non-ferrous alloys (high chromium content). Transfer a 0·1–0·5-g sample to a Teflon beaker and add 5 ml of water, 5 ml of concentrated perchloric acid, 4 ml of concentrated nitric acid, 2 ml of hydrofluoric acid and 5 ml of concentrated hydrochloric acid (if necessary). Cover and heat gently until all of the sample is in solution (additional nitric and hydrochloric acids may be required to obtain complete dissolution). Remove the cover, wash down the sides of the beaker with a small amount of water and evaporate to fumes of perchloric acid. Cool, add approximately 20 ml of water (heat, if necessary, to dissolve salts), transfer the solution to a mercury cathode cell and dilute to approximately 200 ml with water. Electrolyse the resulting solution for 45 min at approximately 10 A, then filter the electrolyte into a 400-ml Pyrex beaker and evaporate to dryness. Wash down the sides of the beaker with a small amount of water, add 8 ml of 12·5*M* sulphuric acid solution and evaporate to fumes of sulphur trioxide. Cool, add 5 ml of water, allow to cool to room temperature and then transfer the resulting solution to a separatory funnel. Add 8 ml of 25*M* hydrofluoric acid solution and proceed with the extraction and determination of vanadium.

RESULTS

Extraction and spectral characteristics of the red vanadium(V)–NBPHA complex

Figure 1 shows the difference between the absorption spectrum of the red complex extracted from a sulphuric acid–fluoride medium and that of the purple complex extracted from a sulphuric acid–chloride medium. The molar absorptivity of the red complex is 428 $\text{l.mole}^{-1}.\text{mm}^{-1}$ at 475 nm, the wavelength of maximum absorption.

Extraction of the red complex (and also the purple complex) was found to be quantitative after four separate batch extractions with 0·1% NBPHA-chloroform

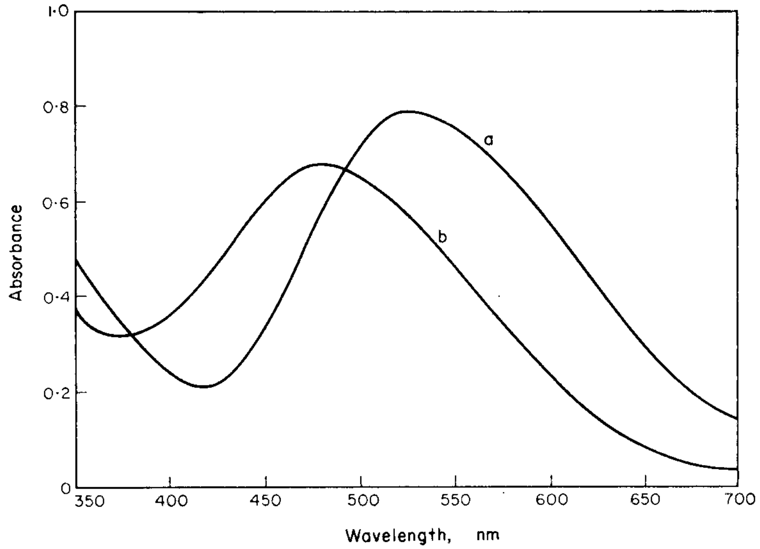

FIG. 1.—Absorption spectra of vanadium (V)-NBPHA complexes. (*a*) Vanadium (V) (100 μg) extracted from 3·25*M* sulphuric acid–1·0*M* sodium chloride medium. (*b*) Vanadium (V) (100 μg) extracted from 2*M* sulphuric acid–1·0*M* potassium fluoride (or hydrofluoric acid) medium. Spectra measured against a reagent blank in 20-mm cell.

solution when 2-min shaking periods were employed. The extracts were found to be stable for at least 24 hr.

Factors influencing formation and subsequent extraction of the red vanadium complex

Effect of oxidant. Potassium permanganate has been employed as oxidant in most methods involving the extraction of the purple vanadium(V)–NBPHA complex from a hydrochloric acid medium. However, the excess of permanganate must be destroyed before the extraction step because this reagent (and other strong oxidizing agents such as potassium dichromate and ceric sulphate) presumably oxidizes NBPHA, producing a yellow extract.[1,2] This destruction can be achieved by reduction with sodium nitrite and subsequent destruction of the excess of nitrite with urea,[1,8] or (with only a small excess) by the addition of the hydrochloric acid needed to maintain the acidity required for extraction.[1]

It has been found in this laboratory, and by other investigators,[6,13] that extraction of the purple complex under these conditions yields low results because some vanadium is reduced in relatively concentrated hydrochloric acid media. In the present work, a similar effect (low and erratic results) occurred when potassium permanganate was used as oxidant, in initial tests involving the extraction of the purple and red complexes respectively from sulphuric acid media containing sodium chloride or potassium fluoride. It was considered that this effect could be associated with the absence of excess of oxidant; consequently, an attempt was made to find an oxidant which could be used in excess, in relatively concentrated sulphuric acid solutions, without producing a yellow extract with NBPHA. Ammonium persulphate was found to fulfill these conditions and subsequent tests performed in both sulphuric acid–sodium chloride and sulphuric acid–potassium fluoride media with an excess of this reagent yielded consistent and reproducible results.

Effect of sulphuric acid concentration. Although the red vanadium(V)–NBPHA complex can be extracted from hydrofluoric acid media alone (0·5–2·5*M*), extraction from sulphuric acid–potassium fluoride (or hydrofluoric acid) solutions was considered more suitable for analytical purposes (*i.e.*, for dissolution procedures). Experiments showed (Table I) that in the presence of 2*M* potassium fluoride or hydrofluoric acid, the extraction of vanadium (as its red complex) is complete from solutions 1·5–5*M*

TABLE I.—EFFECT OF SULPHURIC ACID CONCENTRATION ON THE EXTRACTION OF THE RED VANADIUM COMPLEX

$[H_2SO_4]$, *M*	Absorbance	
	[KF], 2*M*	[HF], 2*M*
0·5	0·083	0·672
1·0	0·595	0·677
1·5	0·667	0·677
2·0	0·673	0·670
2·5	0·669	0·673
3·0	0·674	0·673
3·5	0·674	0·672
4·0	0·666	0·679
4·5	0·676	0·679
5·0	0·675	0·679

Vanadium taken, 100 μg.

or 0·5–5M in sulphuric acid, respectively. An intermediate concentration of 2M was chosen for subsequent work.

Effect of fluoride concentration. Tests carried out to determine the effect of fluoride concentration on the extraction of the red complex from solutions 2M in sulphuric acid showed that extraction is complete from solutions from 0·05 to at least 2M in potassium fluoride or 0·05–6·5M in hydrofluoric acid. Because potassium fluoride, in high concentrations, is insoluble in 2M sulphuric acid media and because tantalum forms an insoluble complex (potassium fluorotantalate) with this reagent, hydrofluoric acid was used in the proposed method. A concentration of 4M was found to be adequate for both extraction and masking purposes.

Effect of diverse ions

Recently, Vita *et al.*[13] have shown that, depending on acidity, various ions [titanium(IV), zirconium(IV), hafnium(IV), niobium(V), tantalum(V), chromium(VI), molybdenum(VI), tungsten(VI), technetium(VII), tin(IV), antimony(III) and antimony(V)] are completely or partially extracted (>50%) with an NBPHA-chloroform solution from hydrochloric acid media; other ions [manganese(II), iron(III), cobalt(II) and nickel(II)] are only slightly extracted (<15%). According to Shendrikar,[14] titanium, zirconium, molybdenum and tungsten are the principal interferents in the determination of vanadium by extraction of its purple NBPHA complex from a hydrochloric acid medium. However, other ions mentioned above (niobium, tantalum, tin, manganese and chromium) have been found to interfere also.[1–3] In the present work, involving extraction of vanadium from 2M sulphuric-4M hydrofluoric acid media, tests were carried out with 10-mg amounts of all of the ions mentioned above (except hafnium and technetium) and various other ions [copper(II) cadmium(II), zinc(II), arsenic(V), bismuth(III) and cerium(IV)]. The results of these tests showed that none of the ions tested, except chromium and cerium, interfered in the extraction and subsequent determination of vanadium. Additional tests performed with 500-mg amounts of niobium, tantalum, molybdenum, tungsten, titanium and zirconium showed that only molybdenum and tungsten interfered at this level by inhibiting the extraction of vanadium. However, up to 50 mg of these ions (present separately) do not interfere in the proposed method, and up to 100 mg can be tolerated if five batch extractions are performed. In these tests (and some of the previous tests) changes in the absorption spectra, detected between 340 and 425 nm, of extracts from niobium, tantalum, molybdenum and tungsten solutions suggested that some co-extraction of these ions occurs. Analysis (approximate) of the extracts confirmed this and showed that the amounts co-extracted, at the 500-mg level, did not exceed approximately 3 mg.

Interference from chromate and ceric ions is avoided in the proposed method by reduction of these ions to the tervalent state with iron(II).[1] Vanadium is also reduced by this reagent but is subsequently re-oxidized to the quinquevalent state with ammonium persulphate; chromium(III) and cerium(III) are not re-oxidized under these conditions (except possibly when silver is present).

Applications

The proposed method was applied to the analysis of a series of synthetic niobium and tantalum samples in which the added vanadium was varied from 0·001 to 0·10%.

TABLE II.—RECOVERY OF VANADIUM BY THE PROPOSED METHOD FROM SYNTHETIC NIOBIUM AND TANTALUM SAMPLES

Matrix	Total V present, %	V found, %
Nb	0·0014	0·0014
	0·0054	0·0055
	0·0104	0·0106
	0·0254	0·0257
	0·0504	0·0510
	0·1004	0·1022
Ta	0·0010	0·0010
	0·0050	0·0051
	0·0100	0·0100
	0·0250	0·0251
	0·0500	0·0502
	0·1000	0·1003

Duplicate determinations of vanadium in the Nb and Ta metals by the proposed method gave average results of 0·0004% and none detected, respectively.

TABLE III.—DETERMINATION OF VANADIUM IN N.B.S. STEEL, CAST IRON AND NON-FERROUS ALLOY SAMPLES

Sample	Nominal composition, %	Certified value and range % V	V found, %
6F Cast iron	0·4 Cr, 0·1 Ti, 0·5 Mn	0·032 (0·027–0·038)	0·031
19G Acid open-hearth steel	0·4 Cr, 0·6 Mn	0·012	0·012
30E Chromium–vanadium steel	0·9 Cr, 0·8 Mn	0·149 (0·146–0·152)	0·146
32E Nickel-chromium steel	0·7 Cr, 1·2 Ni, 0·8 Mn	0·002 (0·001–0·004)	0·0013
36A Chromium–molybdenum steel	2·4 Cr, 0·9 Mo, 0·4 Mn	0·006 (0·005–0·007)	0·0041, 0·0040*
85B Aluminium alloy	0·2 Cr, 4·0 Cu, 1·5 Mg, 0·6 Mn	0·006	0·0069
87A Silicon–aluminium alloy	6·2 Si, 0·2 Ti, 0·1 Cr	<0·01	0·0080
100A Manganese steel	1·7 Mn	0·003	0·0019
101E Chromium–nickel steel	18·0 Cr, 9·5 Ni, 1·8 Mn	0·043 (0·038–0·045)	0·039*, 0·039*
106B Chromium–molybdenum–aluminium–steel	1·2 Cr, 0·2 Mo, 1·1 Al, 0·5 Mn	0·003 (0·002–0·005)	0·0030
111A Nickel–molybdenum steel	1·7 Ni, 0·2 Mo, 0·2 Cr, 0·7 Mn	0·002	0·0020
133 Chromium–molybdenum steel	13·6 Cr, 0·6 Mo, 0·8 Mn	0·020 (0·014–0·025)	0·018*
139 Chromium–nickel–molybdenum steel	0·5 Cr, 0·6 Ni, 0·2 Mo, 0·9 Mn	0·002	0·0016
155 Chromium–tungsten steel	0·5 Cr, 0·5 W, 1·2 Mn	0·014 (0·010–0·022)	0·012
159 Chromium–molybdenum–silver steel	1·0 Cr, 0·4 Mo, 0·1 Ag, 0·8 Mn	0·054 (0·046–0·06)	0·053
160A Chromium–nickel–molybdenum steel	18·8 Cr, 14·1 Ni, 2·8 Mo, 1·6 Mn	0·052	0·050*
161 Nickel–chromium casting alloy	64·3 Ni, 16·9 Cr, 15·0 Fe, 0·5 Co, 1·3 Mn	0·029 (0·023–0·034)	0·029*

* Mercury cathode separation of chromium.

The standard vanadium solution was added directly to the powdered metal samples. It was also applied to cast iron, steel, non-ferrous alloys and standard silicate rocks. The chemical compositions of six of these rocks (G-2–BCR-1), which were obtained from the United States Geological Survey, have not been fully established. The results of these analyses are given in Tables II, III and IV.

TABLE IV.—DETERMINATION OF VANADIUM IN U.S.G.S. STANDARD SILICATE ROCKS

Sample	Vanadium, *ppm*			
	Reported value and range	Average value (Peck‡)	Average value (Suhr§)	This work
G-1 (granite)	16 (10–21)*	15 ± 1	—	16·0
W-1 (diabase)	240 (213–360)*	276 ± 7	—	272, 274
G-2 (granite)	37 (26–60)†	35	39	35·5, 35·5
GSP-1 (granodiorite)	52 (38–67)†	53	53	52·5, 52·5
AGV-1 (andesite)	121 (70–171)†	124	125	121, 122
PCC-1 (peridotite)	31·2 (21–55)†	29	28	22·0, 23·0
DTS-1 (dunite)	18·9 (6–52)†	11	<5	6·0, 6·5
BCR-1 (basalt)	384 (120–700)†	426	420	420, 424

* Fleischer.[15]

† Flanagan.[16]

‡ Average values (spectrophotometric) by L. C. Peck (U.S. Geological Survey, Denver, Colorado reported by Fleischer and Flanagan.

§ Average values (optical spectrography) by N. H. Suhr (Pennsylvania State University, University Park, Pennsylvania) reported by Flanagan.

DISCUSSION

Table II shows that the results obtained for the synthetic niobium and tantalum samples agree favourably with the total calculated amount present. The results obtained (Table III) for National Bureau of Standards samples of cast iron, aluminium and nickel-chromium alloys and different types of steel are in excellent agreement with certificate values. Although not all of the results obtained (Table IV) for the silicate rocks agree with the values reported by Fleischer[15] and Flanagan,[16] they are in reasonably good agreement with all of the average results obtained by Peck and Suhr. Flanagan's values for samples G-2–BCR-1 are the result of the first compilation of data on these rocks and represent the arithmetic mean (of approximately 17–22 values) of widely varying values obtained by different investigators using various methods (optical spectrography, X-ray fluorescence, spectrophotometry). Because of the distribution of these data either above or below Flanagan's reported values, his arithmetic mean values for PCC-1 and DTS-1 may be high, while that for BCR-1 may be low. For example, for DTS-1, 15 results out of 20 are in the range <5–18·9 ppm (mean value), while 10 out of 20 are 11 ppm and lower. Similarly, for PCC-1, 14 results out of 20 are in the range 20–31·2 ppm (mean value). Conversely, for BCR-1, 14 results out of 22 are 384 ppm and higher.

Recently, Dražić-Antonijević *et al.*[17] have suggested that the purple complex extracted from relatively concentrated hydrochloric acid media is a vanadium(V)-NBPHA complex with one co-ordinated chloride ion. Montequi[18] and Majumdar *et al.*[19] have also isolated the compounds $[(C_{13}H_{10}O_2N)_2VO_2H.HCl]$ and $VO(NBPHA)_2Cl$, respectively. Consequently, it is reasonable to assume that the red complex extracted from fluoride media is a corresponding vanadium(V)–NBPHA–fluoride complex. The differences in the absorption spectra, *i.e.*, absorption maxima and molar absorptivities, of the two complexes (Fig. 1) indicate strongly that chloride and fluoride ions react in these systems by co-ordination, not by ion-association. It is probable that vanadium forms similar red fluoro-complexes with other substituted hydroxylamines because the purple complexes, extracted from hydrochloric acid media with chloroform solutions of these reagents, appear to resemble the vanadium–NBPHA–chloride complex; their absorption maxima and molar absorptivities do not differ very greatly.[20–23]

In the initial work involving the extraction of the purple vanadium(V)–NBPHA complex from sulphuric acid–sodium chloride media, extractions were carried out at about 5–15° because it was observed that ammonium persulphate oxidizes chloride ion to chlorine at room temperature. A similar effect cannot occur with fluoride.

In the proposed method, the amount of iron(II) used is sufficient to reduce approximately 10 mg of chromium(VI). A mercury cathode separation in perchloric acid medium is recommended for samples containing larger amounts of chromium, because of the insolubility of chromium(II) salts in sulphuric acid alone and in the sulphuric–hydrofluoric acid medium used for extraction.

The method for niobium and tantalum metals is suitable, without modification, for the determination of small amounts of vanadium in titanium and zirconium metals. It has been employed to determine trace amounts of vanadium in cobalt and nickel arsenides, but, to obtain complete extraction, it was found necessary to increase the concentration of ammonium persulphate. It can also be applied to molybdenum and tungsten metals, if not more than 100 mg of sample are taken and five batch extractions are performed. Tungsten forms the insoluble hydrated trioxide when the recommended dissolution procedure is employed. However, satisfactory solutions can be prepared by using less sulphuric acid and evaporating to near dryness, followed by dissolution of the tungsten trioxide residue in potassium hydroxide solution and addition of the requisite amounts of sulphuric (including that required to neutralize the excess of potassium hydroxide) and hydrofluoric acids.

Priyadarshini and Tandon[2] state that the colour system resulting from the extraction of the purple vanadium(V)–NBPHA complex from hydrochloric acid media obeys Beer's law between the limits of 0·7 and at least 12 ppm of vanadium (17·5–300 μg; 25-ml volume; 10-mm cells). In the present method Beer's law is obeyed for 1–150 μg of vanadium and the calibration curve passes through the origin. Larger amounts were not tested because of the high absorbance of the extract when 20-mm cells are used for measurement. Although the proposed method is slightly less sensitive than methods involving extraction of the purple complex, it is considerably more selective and reasonably specific as far as common ions are concerned.

The method presented in this paper is suitable for samples containing up to 0·15% of vanadium, but material containing larger amounts can also be analysed if smaller samples or suitable aliquots (with the exception of niobium and tantalum metals) of a sulphuric acid solution of the sample are taken.

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Zusammenfassung—Ein Verfahren zur Bestimmung von bis zu 0,15% Vanadium in hochreinem metallischem Niob und Tantal, Gußeisen, Stahl, Nichteisenlegierungen und Silikaten wird beschrieben. Es beruht auf der Extraktion eines roten Komplexes von Vanadium(V) mit

N-Benzoyl-*N*-phenylhydroxylamin in Chloroform aus einem schwefel- und flußsauren Medium, das überschüssiges Ammonpersulfat als Oxidationsmittel enthält. Der molare Extinktionskoeffizient des Komplexes beträgt bei 475 nm, dem Absorptionsmaximum, 428 l mol^{-1} mm^{-1}. Die Störung durch Chrom(VI) und Cer(IV) wird durch Reduktion mit Eisen(II) beseitigt. Häufig vorkommende Ionen, auch große Mengen Titan, Zirkonium, Molybdän und Wolfram stören nicht.

Résumé—On décrit une méthode pour doser jusqu'à 0,15 per cent de vanadium dans les niobium et tantale métalliques de haute pureté, la fonte, l'acier, des alliages non ferreux et des silicates. La méthode proposée est basée sur l'extraction d'un complexe rouge vanadium(V)-*N*-benzoyl *N*-phénylhydroxylamine en chloroforme d'un milieu acide sulfurique-acide fluorhydrique contenant un excès de persulfate d'ammonium comme oxydant. Le coefficient d'absorption moléculaire du complexe est 428 l.mole^{-1}.mm^{-1} à 475 nm, la longueur d'onde du maximum d'absorption. On élimine l'interférence du chrome(VI) et du cérium(IV) par réduction au fer(II). Les ions communs, y compris de grandes quantités de titane, zirconium, molybdène et tungstène ne gênent pas.

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RELATIVE SENSITIVITY OF RARE EARTH ELEMENTS IN SPARK-SOURCE MASS SPECTROMETRY*

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Summary—A method for calculating the relative sensitivity factors for the rare earth elements in geological material is outlined. A close correlation is found between the relative sensitivity factors calculated and isotopic mass and the first ionization potential for the elements. The points are grouped in the vicinity of a regression line, which may be used to determine the relative sensitivity factors for all the rare earth elements.

THE SENSITIVITY factors of rare earth elements relative to rhenium given by Nicholls *et al.*[2] vary between 14·0 and 28·0. The variation of these relative sensitivity factors has no straightforward relation to mass number.

In the present work the relative sensitivity factors of the rare earth elements were studied in more detail in two standard rocks, W-1 and ASK Larvikite, and two quaternary clays from Åserum and Rødberg, Norway. The rare earth concentrations were also determined by neutron-activation analysis.[3–5] The relative sensitivity factors for the lanthanide elements and yttrium are calculated on the basis of mass spectrometric and neutron-activation analysis.

EXPERIMENTAL

The mass spectrometer was a GEC/AEI MS 702 fitted with Norbeck sample holders. The powdered samples were mixed with equal amounts of Ringsdorffwerke RWO graphite, pressed, and the electrodes evacuated to <1 μbar. Working pressures in the analyser region and in the source region were 53 pbar and 5·9 nbar respectively. The exposure conditions have been described by Taylor.[6] The data used were similar to those applied by Nicholls *et al.*[2] The densities of each line were measured by a modified Joyce-Loebl recording microdensitometer.

Rhenium satisfies the criteria for an internal standard element listed by Taylor[6] and Nicholls *et al.*[2] A solution of rhenium (Johnson Matthey "Specpure" potassium perrhenate) was added to the powdered sample at ppm level. This method is satisfactory for the fine-grained clay samples, though generally not for powdered rock samples.

RESULTS

The rare earth concentrations in W-1, ASK Larvikite, Åserum and Rødberg clay, determined by neutron-activation analysis, are listed in Table I. The data for W-1 and ASK Larvikite represent average values (La, Ce, Nd, Sm, Eu, Tb and Lu) of 10 and 6 replicate analyses respectively and (Gd, Dy, Ho and Tm) of 4 replicate analyses. The relative standard deviations for the concentrations of Nd, Tb, Ho, Yb and Lu are 10–30% and are larger for Gd. The data for Åserum clay represent one analysis while the data for Rødberg clay represent the mean of two analyses. Duplicate analyses agreed within 10% for La, Ce, Sm and Eu and within 15% for Nd, Gd and Tb.

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* Contribution to the Numedal project.[1]

TABLE I.—CONCENTRATIONS (*ppm*) OF RARE EARTH ELEMENTS IN W-1, ASK LARVIKITE, ÅSERUM AND RØDBERG CLAYS

	W-1[4]	ASK Larvikite[4]	Åserum clay[3]	Rødberg clay[5]	Isotope used[5]	Isotopic abundance[7], %	Ionization energy[7] *eV*
Y	24[8]		40		89	100	6·38
La	10·9	120	53	97	139	99·91	5·61
Ce	27·4	229	143	190	140	88·48	5·60
Nd	16·4	70	88	18·1	143	12·17	5·51
Sm	3·36	13·1	11	9·4	149	13·83	5·60
Eu	1·1	5·5	1·44	1·75	153	52·18	
Gd	4·3	15	11	8·4	158	24·87	6·16
Tb	0·7	2·0	1·44	0·93	159	100	5·98
Dy	4·4	10·6	7·0		161	18·88	6·8
Ho	1·0	2·7	1·48		165	100	
Er			4·1		166	33·41	6·08
Tm	0·7	0·97	0·56		169	100	
Yb	2·4	4·13	4·0		174	31·84	6·2
Lu	0·4	0·60	0·6		175	97·41	
Re					187	62·93	7·87

The literature data for the ionization energies for the rare earth elements vary. The relative sensitivity factors were determined from equation (1):

$$C_E = C_S \times \frac{Exp_S}{Exp_E} \times \frac{I_S}{I_E} \times \frac{1}{R} \tag{1}$$

C_E = content of element E in electrode analysed (in ppm).

C_S = content of a second element S, the internal standard element (in ppm).

Exp_S = exposure (in ncb) required to give a line of chosen density for a chosen isotope of element S on a photographic plate.

Exp_E = exposure in the same units required to give a line of the same chosen density for a chosen isotope of element E on the same photographic plate.

I_S = isotopic abundance of the chosen isotope of S.

I_E = isotopic abundance of the chosen isotope of E.

R = the relative sensitivity factor, introduced as a measure of sensitivity of total recording procedure for line of element E used compared with sensitivity for line of element S used.

In Table II the calculated *R*-factors are tabulated together with the data obtained by Nicholls *et al.*[2] The *R*-factors for Eu are remarkably high. Interference with ^{153}Eu results from ^{137}BaO$^+$ with mass 153.

Multiple carbon atoms interfere at line 169 and make it impossible to determine R_{Tm} by this method. The neutron-activation results for the Gd content in the standard rocks show great variations. *R*-factors based on these values were not calculated. The intensities of the mass spectral lines for Lu were too weak to give reliable calibration curves for this element.

When the relative sensitivity factors calculated are plotted *vs.* isotopic mass and *vs.* the first ionization potential the points are grouped near a regression line, as illustrated in Figs. 1 and 2. The data for W-1 and Åserum clay are the most complete. The values for europium are not incorporated in the calculations.

The regression lines were calculated by least-squares, and a close correlation was found in both cases, as shown in Table III.

Table II.—The relative sensitivity factors for the rare earth elements

	W-1	ASK Larvikite	Åserum clay	Rødberg clay	Obtained by Nicholls *et al.*[2]
R_{Y}	8·7		7·0		14·0
R_{La}	10·4	8·5	9·2	8·2	18·0
R_{Ce}	7·6	9·0	7·7	8·1	
R_{Nd}	10·5		10·4	11·7	24·1
R_{Sm}	10·2	10·1	8·3	9·7	
R_{Eu}	24·4	25·0	16·2	10·5	28·0
R_{Gd}			7·9	8·5	26·4
R_{Tb}	10·5	7·7	6·2	7·6	15·5
R_{Dy}	7·1	3·0	8·2		22·6
R_{Ho}	4·8	3·5	4·4		15·5
R_{Er}			6·0		14·0
R_{Yb}	6·2	4·7	5·25		
R_{Lu}					16·4
R_{Re}	1·0	1·0	1·0	1·0	1·0

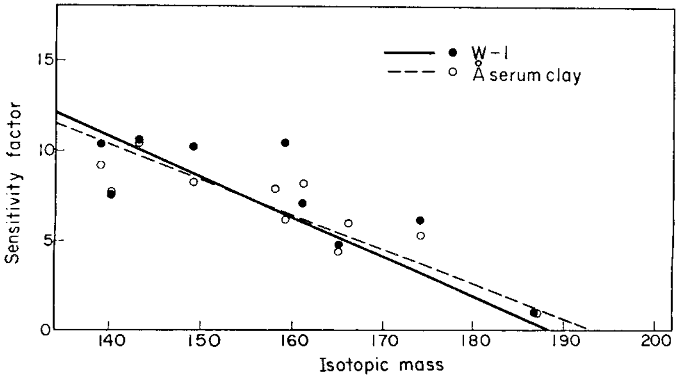

Fig. 1.—Variation of sensitivity factor with isotopic mass.

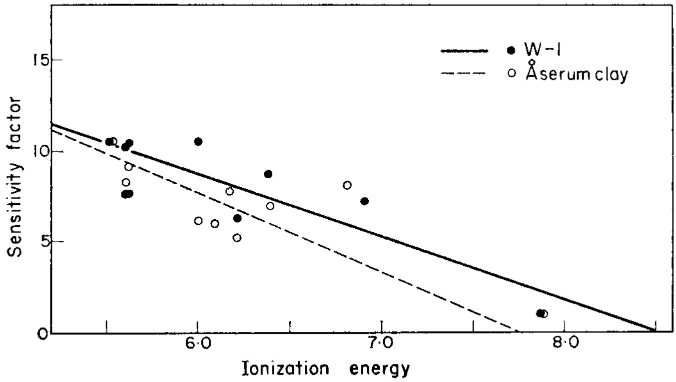

Fig. 2.—Variation of sensitivity factor with ionization energy.

TABLE III.—THE REGRESSION LINES $Y = AX + B$

		A	B	Std. devn. of X	Std. devn. of Y	Correlation coefficient
W-1	1	−4·14	188·9	$4·1 \times 10^{-9}$	97·96	−0·8247
	2	−3·54	29·9	$-1·2 \times 10^{-9}$	2·44	−0·8818
Åserum	1	−5·05	192·5	0	53·93	−0·8834
clay	2	−2·91	24·9	0	2·35	−0·8097

1. For the relative sensitivity factor *vs.* isotopic mass.
2. For relative sensitivity factor *vs.* ionization energy.

The relative sensitivity factors for all the lanthanide elements are determined from the regression line provided that the R-factors are on this line.

Correction for interference of $^{137}BaO^+$ with ^{153}Eu is made by using the intensity of line 154, which results from ^{154}Sm, ^{154}Gd and $^{138}BaO^+$, combined with the isotopic abundances of the Ba, Sm and Gd isotopes.[7]

If the intensities of lines 153 and 154 were caused by monoisotopic elements, the concentrations of these elements in the sample, C_{153} and C_{154}, would be:

$$C_{153} = C_S \times \frac{Exp_S}{Exp_{153}} \times \frac{I_S}{100} \times \frac{1}{R_{153}} \tag{2}$$

and

$$C_{154} = C_S \times \frac{Exp_S}{Exp_{154}} \times \frac{I_S}{100} \times \frac{1}{R_{154}} \tag{3}$$

where R_{153} and R_{154} are the relative sensitivity factors for isotopes with masses 153 and 154. The R-factors are taken from the regression line. The intensity of line 153 results from $^{137}BaO^+$ and ^{153}Eu:

$$C_{153} = C_{^{137}BaO^+} + C_{^{153}Eu} \times (52.18/100) \tag{4}$$

and the intensity of line 154 results from Sm and Gd in addition to barium oxide:

$$C_{154} = C_{^{138}BaO^+} + C_{^{154}Sm} \times (22.71/100) + C_{^{154}Gd} \times (2·15/100) \tag{5}$$

The amount of interfering $^{137}BaO^+$ is calculated by using the isotopic abundance of Ba and the amount of $^{138}BaO^+$ [which is calculated from equation (5)]:

$$C_{^{137}BaO^+} = C_{^{138}BaO^+} \times (11·32/77·66) \tag{6}$$

The equations are combined in an expression for the europium concentration, C_{Eu}:

$$C_{Eu} = \{C_{153} - [C_{154} - (C_{Sm} \times 22·71 + C_{Gd} \times 2·15)/100] \times 11·32/77·60\} \times 100/52·18 \tag{7}$$

To get better evidence for the relation between the relative sensitivity factors and isotopic mass, the polyisotopic lanthanides were studied. Solutions of Sm, Dy and Gd, were added to graphite, dried and analysed. The relative sensitivity factors calculated for the different isotopes of a particular element decreased as the isotopic mass increased.

DISCUSSION

Yttrium is chemically similar to the lanthanide elements. The calculated sensitivity factor for yttrium is near those for dysprosium and holmium. This indicates that the sensitivity factors are not primarily a function of isotopic mass. Either the ionization energy, or the ionization potential, is the dominating factor. However, the literature values for the ionisation energies of the lanthanides are unreliable. The dependence on ionization potential has been mentioned by Taylor.[6] Elements with low ionization potentials give the highest sensitivity while elements with high ionization potentials give poorer sensitivity. The ionization energies increase from lanthanum to lutetium.

The Saha-Langmuir equation in its modified form, when the ionization potential of the evaporating atoms exceeds the maximum electronic work function of the polycrystalline surface, gives the total positive ion current I^+ from the surface as[9]

$$I^+ = eA^* \exp (e/kT)(\phi^* + \psi - \mathrm{I})$$

where

$$A = An_0 \sum_n F_n \exp (e/kT)(\phi_n - \phi^*)$$

where e is the charge of the electron; A is a constant which includes the statistical weights, the reflection coefficients of the ions and neutral atoms and the transmission constant of the lens system of the ion source; n_0 is the number of neutral particles incident per cm^2 of the n-th fraction of the surface of area F_n and work function ϕ_n per sec; ϕ^* is the effective work function of the surface, its value lying between the maximum and minimum values of work function of the polycrystalline surface; k is the Boltzmann constant; T is the absolute temperature of the surface; I is the ionization potential of evaporating atoms and ψ is a function of the electric field strength at the surface.

From the constant A in the Saha-Langmuir equation it is evident that the ionization potential of an isotope is a function of its mass. Most of the parameters in the equation are unknown variables. Until these factors are known it is impossible to determine the ionization potentials with the desired accuracy. When the ionization energies are accurately determined they can be used to calculate the relative sensitivity factors for trace elements.

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Zusammenfassung—Eine Methode zur Berechnung der relativen Empfindlichkeitsfaktoren der seltenen Erdelemente in geologischem Material wird skizziert. Es wird eine enge Beziehung zwischen den berechneten Empfindlichkeitsfaktoren und der Nuklidmasse und dem ersten Ionisationspotential der Elemente gefunden. Die Punkte gruppieren sich in der Nähe einer Regressionslinie, die zur Ermittlung der relativen Empfindlichkeitsfaktoren aller seltenen Erdelemente dienen kann.

Résumé—On indique une méthode pour calculer les facteurs de sensibilité relatifs pour les éléments des terres rares dans des matières géologiques. On trouve une relation étroite entre les facteurs de sensibilité relatifs calculés et la masse isotopique et le premier potentiel d'ionisation pour les éléments. Les points sont groupés au voisinage d'une ligne de régression, que l'on peut utiliser pour déterminer les facteurs de sensibilité relatifs pour tous les éléments des terres rares.

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INDIRECT DETERMINATION OF FLUORIDES BY THE EDTA TITRATION OF SAMARIUM

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Summary—Fluorides are determined by the back-titration of excess of samarium with EDTA to the canary yellow end-point of Methylthymol Blue. The fluoride is precipitated and digested in a solution buffered at pH 2·5–3·0 with monochloroacetate buffer. After digestion, the pH is adjusted to 5·6–5·8 with pyridine and the excess of samarium is back-titrated in the presence of the precipitate, for samples with small quantities of fluoride. The procedure was used to analyse simple fluorides, fluoroborates and some other fluoro-complexes.

THE NEED to determine the total fluoride in fluoride–fluoroborate mixtures ranging from moderately concentrated to very dilute solutions required study of the system. Unsatisfactory analytical results were obtained with different procedures such as the titration with thorium nitrate,[1] the pyrolytic-cerium technique,[2] the Winter and Willard distillation method,[3] and the gravimetric lanthanum fluoride method[4] because of boron complex interference. In addition, in the pyrolytic-cerium technique,[2] the end-point colour change for the arsenazo-Cresol Red indicator, from pale red to yellow-orange, was quite inconclusive. Precipitation of the fluoride as calcium fluoride was not used, because of the gelatinous nature of the precipitate and difficulties previously experienced with filtering.

It was found possible to precipitate relatively small quantities of the very insoluble samarium fluoride as a granular easily filterable precipitate. Larger quantities of fluoride produced the expected gelatinous precipitate[5] unless precipitated carefully and digested for periods of one or more hours. This precipitate was found to be essentially insoluble in low concentrations of EDTA. A back-titration procedure for small quantities of total fluoride was therefore developed; the fluoride is precipitated as samarium fluoride (SmF_3) and the excess of samarium ion is titrated with EDTA by using Methylthymol Blue as the indicator. The back-titration is performed in the presence of the precipitate unless the latter is large. Fluoroborates and fluorosilicates are analysed in the same manner. For fluorostannates, thioglycollic acid was used to complex the tin.

EXPERIMENTAL

Reagents

EDTA solution, 0·010*M*. Standardized against standard yttrium solution.

Methylthymol Blue indicator solution, 0·05% *w/v*.

Yttrium stock solution, 10·00 *mg/ml*. Dissolve 2·5398 g of yttrium oxide (Y_2O_3, 99·9999% pure, ignited to constant weight) in 35 ml of hydrochloric acid (1 + 1) and dilute to 200 ml. For standard working solution, 0·500 mg/ml, dilute 10·00 ml of the stock solution to 200·0 ml with 1*M* hydrochloric acid.

Samarium chloride stock solution. Dissolve approximately 10·5 g of samarium trichloride in 0·1*M* hydrochloric acid and dilute to 250 ml with the same acid; 1 ml is equivalent to about 6 mg of fluoride. For lower amounts of fluoride, dilute the stock solution 20-fold with 0·2*M* hydrochloric acid. Standardize these solutions against the standard EDTA solution. Samarium oxide, ignited, and then dissolved in hydrochloric acid (1 + 1), can be used in place of the Y_2O_3 and $SmCl_3$.

Pyridine solution, 50% *v/v*. Prepared from analytical-grade pyridine and demineralized water.

Monochloroacetate buffer. Dissolve 47·2 g of monochloroacetic acid and 10 g of sodium hydroxide in water and dilute to nearly 500 ml. If the pH is not between 2·5 and 3·0, adjust with a little of the solid acid or alkali, as needed.

Apparatus

Semimicro burettes, 5 and 10 ml, were used; stainless steel No. 24 hypodermic needles were used as tips for the EDTA titration. Platinum tips were used for measuring the acidic samarium solutions.

Procedure

Samples analysed by this procedure were received in solution, or as solids which dissolved in water or dilute hydrochloric acid.

To the dissolved sample or an aliquot, slowly add an excess of standard samarium chloride solution, approximately 1·5–2 times the expected stoichiometric amount. Adjust the pH to 2·5–3·0 with 0·2*M* hydrochloric acid or 4*M* ammonia. Should the solution be strongly acidic, dilute sodium hydroxide solution may be used in the initial phase of the pH adjustment. Add 10 ml of the monochloroacetic buffer. Digest on a sand-bath at approximately 90° for 30 min or more, then cool to room temperature. The time for digestion will depend on the amount of precipitate. Adjust the pH to 5·6–5·8 with the pyridine solution, added dropwise as the desired pH is approached. Pyridine is used since rare earth fluorides are slightly soluble in ammonium salt solutions. Add 1 ml of Methylthymol Blue indicator and back-titrate the excess of samarium with standard EDTA solution to the yellow end-point colour.

Filtering is not necessary for samples containing low quantities of fluoride; the back-titration is carried out in the presence of the precipitate. The precipitate from larger samples interferes with the visibility of the end-point colour change. Samples containing 20 mg or more fluoride should be diluted to a specific volume and aliquots taken for the precipitation and subsequent titration. Alternatively, all the fluoride can be precipitated, and digested, then the precipitate be permitted to settle after diluting to volume; after this aliquots of the clear solution are taken for the back-titration.

RESULTS AND DISCUSSION

Indicator

For the samarium–EDTA titration, Methylthymol Blue yields a sharp colour change from blue to canary yellow at the end point. Two or three drops (1 drop = 0·01 ml) of 0·01*M* EDTA produces the colour change. This end-point is far superior to that for indicators such as arsenazo-Cresol Red or Eriochrome Black T. In the presence of the samarium fluoride precipitate, a short warning of the approaching end-point is indicated by a colour change from blue to gray, which is followed by the yellow. About two drops of 0·01*M* titrant are needed for each change in colour. When 0·1*M* EDTA is used, the intermediate gray is not observed. The curve for spectrophotometric titration with samarium fluoride present did not indicate the change to gray; apparently this change is due to the light-scattering effect of the precipitate.

The spectrophotometric titration showed sharp deflections in the titration curves for 0·1 and 0·01*M* EDTA but a gradual change for the titration with 0·001*M* EDTA. The last is not satisfactory for visual titrations because the end-point is not well defined.

Traces of iron interfere with the titration, giving a change from blue to a reddish colour. The iron forms a more stable complex with the indicator than with EDTA.

Range and reproducibility

Visual titrations were carried out in the range from 1 to 6 mg of fluoride from sodium fluoride and sodium fluoroborate. Various mixtures totalling from 3 to 4 mg of fluoride were also titrated. At the 1-mg fluoride level, based on 14 samples, the standard deviation was approximately 16 μg and the average relative error was $-3{\cdot}0\%$. At the 2, 4 and 6-mg quantities, based on 12 samples, the standard deviations and relative errors were approximately 17, 7 and 9 μg, and $-9{\cdot}0\%$, $-0{\cdot}1_5\%$, and

—0·1$_2$%, respectively. For 20 mixed samples the standard deviation was 9 μg and the relative error was —0·3$_4$%. The individual results for this sample range are shown in Table I. Results for quantities in the range of 100–200 mg of fluoride are given later, in Table IV.

TABLE I.—RANGE AND REPRODUCIBILITY*

Number of titrations	Sample, *mg* F, taken as			Time of digestion, *min*	F found, *mg*	Relative error, %	Std. devn., *μg*
	NaF	$NaBF_4$	Total				
6	0·994$_5$			30	0·958	−3·6	34
4	1·989			30	1·959	−1·5	13
4	3·978			30	3·970	−0·2	7
4	5·967			30	5·950	−0·3	14
4	0·994$_5$			60	0·969	−2·5	5
4	1·989			60	0·976	−0·7	16
4	3·978			60	3·974	−0·1	8
4	5·967			60	5·982	+0·3	6
4		0·929$_7$		30	0·904	−2·9	8
4		1·859		30	1·849	−0·5	21
4		3·719		30	3·714	−0·1	7
4		5·578		30	5·556	−0·3	9
4	0·994$_5$	1·859	2·854	30	2·838	−0·6	8
4	1·989	1·859	3·848	30	3·866	+0·5	7
4	1·989	0·929$_7$	2·919	30	2·901	−0·6	6
4	2·984	0·929$_7$	3·914	30	3·898	−0·4	12
4	0·994$_5$	2·790	3·785	30	3·764	−0·6	11

* 0·01*M* EDTA, visual titrations.

The results for sodium fluoroborate and various ratios of sodium fluoride and sodium fluoroborate indicate that the precipitation of samarium trifluoride quantitatively breaks up the fluoroborate complex.

It is to be noted that the relative errors are generally negative. Since the EDTA was standardized directly against yttrium oxide this indicates that the negative values are due to slight solubility of the precipitate (assuming titration to the correct end-point). In some experiments in which the samples were permitted to stand after titration, the blue colour would begin to return in a half-hour or so, indicating some solubility of the precipitate in the slight excess of EDTA. Indirect standardization of the EDTA against 1–2 mg of fluoride, precipitated as samarium fluoride, would reduce the relative error in this concentration range.

Digestion time

A 30-minute digestion was used in obtaining most of the results included in the tables. In a brief study to determine the effect of time on completeness of precipitation and crystal growth with sodium fluoride and sodium fluoroborate, the difference for 30- and 60-min digestion periods was found to be insignificant. However, for some of the more stable complexes and precipitates, or larger samples, long digestion times were necessary.

Delayed back-titration

Samarium fluoride, precipitated from sodium fluoride samples, after digestion was left remaining in the buffered solution at pH 2·5–3·0 for 0–20 hr before titration. There was no significant change in the relative errors.

Effect of pH

A pH range of 2·5–3·0 was found satisfactory for the precipitation of samarium fluoride from the solution containing fluorides and fluoro-complexes. There was little variation in error with pH changes from 2·5 to 3·5 for sodium fluoride, but the error is relatively large at pH 3·5 for the fluoroborate, Table II. The rapidly increasing positive error associated with pH increase results from the hydrolysis of the samarium ion and its subsequent precipitation as the hydroxide. The negative error increased rapidly with an increase in acidity, Table II. For acid samples, the errors were more negative if the precipitate was permitted to stand before titration. This increasing error is thought to be due to the formation and possible loss of the weak hydrofluoric acid ($K_a = 7{\cdot}2 \times 10^{-4}$) in the presence of the strong hydrochloric acid. In simple experiments to detect evolution of hydrogen fluoride, slight etching was found on the watch-glass covers.

TABLE II.—EFFECT OF pH ON PRECIPITATION OF SmF_3

	NaF*			NaBF$_4$†		
pH 6	F found, *mg*	Error		F found, *mg*	Error	
		mg	% Rel.		*mg*	% Rel.
1·75	3·811	−0·167	−4·2	3·781	+0·062	+1·7
2·00	3·830	−0·148	−3·7	3·740	+0·021	+0·6
2·25	3·884	−0·094	−2·4	3·727	−0·008	+0·2
2·50	3·974	−0·004	−0·1	3·714	−0·005	−0·1
2·75	3·975	−0·003	−0·1			
3·00	3·977	−0·001	−0·0	3·721	+0·002	+0·1
3·25	3·965	−0·013	−0·3			
3·50	3·968	−0·010	−0·3	3·674	−0·045	−1·2
4·00	4·004	+0·026	+0·7	3·563	−0·156	−4·2
4·50	4·089	+0·111	+2·8	3·537	−0·182	−4·9
5·00	4·116	+0·138	+3·5	3·225	−0·494	−13·3
5·60	4·154	+0·176	+4·4	3·105	−0·614	−16·5

* 3·978 mg of F taken as NaF.
† 3·719 mg of F taken as NaBF$_4$.

There was little error when the samarium fluoride was precipitated from sodium fluoroborate solution at pH 2·5–3·0, Table II. However, for the more acidic solutions the error was positive, not negative as observed for the sodium fluoride solutions. As the acidity decreased the negative error increased very rapidly, which is in contrast to the pattern observed for the sodium fluoride solutions. The pH range 2·5–3·0 was found to be satisfactory for the digestion of other fluoro-compounds such as fluorosilicate and fluorostannate.

The samarium fluoride obtained from low concentrations of fluoride ion at the proper pH was a granular precipitate which could be filtered off easily. With higher concentrations and more rapid precipitation, the precipitate was colliodal in nature and required more digestion time.

Additional fluoride compounds

The analytical results for some additional fluoro compounds and larger samples (treated solution aliquots) are summarized in Table III. Thioglycollic acid was used to complex the tin.

TABLE III.—ADDITIONAL COMPLEX FLUORIDES

Number of aliquots	Compound	Sample, *mg*		Digestion, *min*	Error		Std. devn., *μg*	Comments
		Taken	Found		*mg*	% Rel.		
4	NaF	9·945	9·950	90	+0·005	+0·05	7	
4	$NaBF_4$	9·298	9·294	90	−0·004	−0·05	5	
4	SnF_2	4·000	3·998	30	−0·002	−0·05	8	15 drops thioglycollic acid before digestion
4	SnF_2	10·000	9·994	60	−0·006	−0·06	4	15 drops thioglycollic acid before digestion
6	Na_2SiF_6	4·000	3·991	30	−0·009	−0·22	6	
4	Na_2SiF_6	9·970	9·941	90	−0·029	−0·29	10	filtered off ppte. before titration
4	K_2SnF_6	4·290	4·286	90	−0·004	−0·09	13	15 drops thioglycollic acid before digestion
4	K_2SnF_6	6·890	6·895	90	+0·005	+0·07	11	

TABLE IV.—INDIVIDUAL SOLID FLUORIDES

Compound	Number of samples	Range of sample weight, *mg*	Mean % fluoride		% Error		Std. devn, %	Comments
			Theory	Found	Abs.	Rel.		
NaF	4	47·5–68·8	45·25	45·1$_7$	−0·0$_8$	−0·2	0·11	
KF	4	435·0–558·2	32·70	32·7$_8$	+0·0$_8$	+0·3	0·33	
Na_2SiF_6	8	132·2–323·7	60·62	60·4$_6$	−0·1$_6$	−0·3	0·02	
K_2SnF_6	8	172·5–415·2	35·75	35·7$_2$	−0·0$_3$	−0·1	0·02	Add thioglycollic acid to complex Sn
SnF_2	8	231·4–415·2	24·35	24·2$_5$	−0·1$_0$	−0·4	0·00$_6$	
CaF_2	4	44·0–68·7	48·67	48·6$_9$	+0·0$_2$	+0·0	0·07	Dissolve with 2 ml of 5% H_3BO_3 and 10 ml of 0·5*M* HCl at 90°. Then digest ppte. 90 min.
MgF_2	4	33·0–68·7	60·98	61·0$_3$	+0·0$_5$	+0·1	0·09	
TiF_4	8	102·5–358·0	61·34	61·3$_8$	+0·0$_4$	+0·1	0·06	Treat fluoride solutions of Fe, Co, Ni, Ti with 40% NaOH to precipitate cation as hydroxide, filter, then treat sample as NaF.
CoF_3	4	98·4–220·3	49·17	46·0$_0$	−3·1$_7$	−6·5	0·00$_5$	
CoF_3*	4	58·5	49·17	48·9$_4$	−0·1$_3$	−0·3	0·02	
FeF_3	8	68·3–163·3	50·51	32·1$_3$	−18·4	−36	0·02	
FeF_3*	4	50·0	50·51	50·4$_5$	−0·0$_6$	−0·1	0·07	
SbF_3	6	159·6–451·4	31·89	30·3$_9$	−1·50	−5·0	0·02	
$AgBF_4$	6	235·7–316·2	39·03	37·1$_2$	−1·91	−4·9	0·11	Ag separated as AgCl
$AgBF_4$*		100·0	39·03	38·9$_7$	−0·06	−0·2	0·08	
$NaAsF_6$†					Very low			

* Solutions containing the elements in stoichiometric ratio corresponding to the nominal compound. Used to determine probability of correct results being obtained for commercial compounds FeF_3, CoF_3, and $AgBF_4$ if these were pure.

† As(III) did not interfere, but reduction of As(V) to As(III) was incomplete.

The analyses of a number of relatively large individual solid samples of different fluoro compounds are summarized in Table IV. Several of these compounds are highly deliquescent or unstable in the presence of moisture and were handled in a dry-box.

When stable fluorides such as calcium and magnesium fluorides were dissolved in dilute hydrochloric acid low results were obtained. It was found that the addition of boric acid, which apparently formed the fluoroborate, prevented the loss of the fluoride as hydrogen fluoride. It was possible to dissolve calcium and magnesium fluorides in samarium solution at pH 2·5 but long digestion periods were required, of the order of 16–24 hr, and the results were slightly low. The use of fusion with sodium carbonate–potassium carbonate mixture (1:1) resulted in fluoride values from 2% to 5% low.

The low results but reasonably good precision for the compounds cobalt(III) fluoride, iron(III) fluoride, antimony fluorides, and silver fluoroborate indicated the compounds were not pure. This finding was confirmed when solutions with the stoichiometric ratio of fluoride ion to cation were prepared and permitted to stand before analysis.

Arsenic(III) did not cause interference, but with the fluooarsenate ion the need to use strong reducing agents made the analysis impossible.

Stable organic fluorides can be analysed after hydrolysis in concentrated sodium hydroxide solution or decomposition by fusion with sodium. It was also found that fluorophosphate compounds required treatment with alcoholic potassium hydroxide.[5]

Diverse ions

The addition of elements that complex with EDTA only in a relatively basic solution, Mg, Ca, Sr and Ba, has no interference effect on the procedure. Elements such as Fe, Co, Ni, Cu, Pb and Zn that react with EDTA at pH 5·6 will interfere and so will those that form strong fluoride complexes, *e.g.*, Fe, Al, Sn, Zr. Iron, cobalt and nickel were separated as the hydroxide. Tin was complexed with thioglycollic acid and prevented interference. However, sulphanilic acid did not release the fluoride from the aluminium fluoride complex.

Bismuth, antimony and arsenic(III) do not cause interference. However, more precise results were obtained when the heavy white precipitate from hydrolysis was removed by filtering.

Most simple anions do not interfere, but phosphates and sulphates will interfere by complexing with the samarium.

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Zusammenfassung—Flouride werden durch Rücktitration von überschüssigem Samarium mit EDTA bis zum kanariengelben Endpunkt von Methylthymolblau bestimmt. Das Fluorid wird aus einer mit Monochloracetatpuffer auf pH 2,3–3,0 gepufferten Lösung gefällt und digeriert. Nach dem Digerieren wird der pH mit Pyridin auf 5,6–5,8 gebracht und das überschüssige Samarium bei kleinen Fluoridmengen in Gegenwart des Niederschlags zurücktitriert. Die Vorschrift wurde zur Analyse von einfachen Fluoriden, Fluoroboraten und einigen anderen Fluorokomplexen verwendet.

Résumé—On dose les fluorures par le titrage en retour d'un excès de samarium avec l'EDTA jusqu'au point de virage jaune canari du bleu de méthylthymol. Le fluorure est précipité et digéré dans une solution tamponnée à pH 2,5–3,0 avec un tampon monochloracétate. Après digestion, on ajuste le pH à 5,6–5,8 avec la pyridine et l'excès de samarium est titré en retour en la présence du précipité pour des échantillons avec de faibles quantités de fluorure. La méthode a été utilisée pour analyse des fluorures simples, des fluoborates et quelques autres fluorocomplexes.

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INFLUENCE OF pH IN FLUORESCENCE AND PHOSPHORESCENCE SPECTROMETRIC ANALYSIS*

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Summary—An account is given of the theory of the effect of pH changes on fluorescence and phosphorescence of organic species which exhibit acid–base properties, and of the practical applications of the effect.

THE USE of fluorimetry and phosphorimetry in organic analytical and bioanalytical procedures has increased considerably in recent years.[1] Because many organic molecules have one or more prototropically dissociable groups, the pH of the solution in which luminescence is observed will influence the characteristics of the luminescence.[2] In fact, both the frequency and the intensity of luminescence from organic acids and bases are pH-dependent.

The frequency shift of molecular luminescence, observed when pH is varied, is due to the conversion of the organic acid into its conjugate base in both the ground and excited states, and the difference between the dissociation constants of the organic acid in the ground state and in the excited states from which luminescence originates. The relationship between the dissociation constants is given, approximately, by the Förster equation[3]:

$$\mathrm{p}K - \mathrm{p}K^* = \frac{hc}{2{\cdot}303kT}(\bar{\nu}_a - \bar{\nu}_b); \tag{1}$$

where pK and pK^* are the logarithms of the reciprocals of the dissociation constants of the organic acid in its ground state and in the excited state from which luminescence originates (the lowest excited singlet state in the case of fluorescence and the lowest excited triplet state for phosphorescence), respectively; h is Planck's constant, k is the Boltzmann constant; c is the velocity of light and $\bar{\nu}_a$ and $\bar{\nu}_b$ are the frequencies (in cm^{-1}) of the 0—0 vibronic band in the luminescence spectra of acid and its conjugate base (if both species are luminescent), respectively.

pH DEPENDENCE OF FLUORESCENCE

In analytical applications, fluorescence is most often observed in fluid solution (aqueous or non-aqueous solutions at room temperature), in which case the rates of association and dissociation in the lowest excited singlet state are usually greater than or comparable to the rate of fluorescence of the excited species ($\sim 10^8$ sec^{-1}). In this case, prototropic equilibrium is at least partially established within the lifetimes of the lowest excited singlet states of acid and conjugate base.[4] Owing to the large difference in electronic dipole moment between a molecule in its ground and lowest excited singlet state, the pK^* for the lowest excited singlet state is usually quite different

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from the pK of the ground state. For phenols, aromatic amines and aromatic mercaptans, the lowest excited singlet state is several orders of magnitude more acidic than the ground state of the same molecule. For carboxylic acids, aromatic aldehydes and ketones and aromatic ring heteroatoms, the lowest excited singlet state is considerably more basic than the ground state.[2] As a result, the shifting of the frequency of fluorescence, due to conversion of the excited acid into excited conjugate base, generally occurs at a pH (or Hammett acidity function, H_0) very different from that at which the shifting of the absorption spectrum (due to conversion of the ground state acid into ground state conjugate base) occurs. Consequently, it is possible to excite a solution which has a pH such that only the acid or its conjugate base is present and therefore only one species can absorb the exciting radiation, and yet observe the fluorescence from both the excited acid and its conjugate base. Conversely, it is possible to excite the solution with pH $\sim$ pK so that the acid and its conjugate base are both excited and then observe fluorescence from only one excited species. On the other hand, if only one member of the conjugate excited pair is fluorescent, it would be possible to excite only the ground state of that species and yet observe no fluorescence, or only part of the maximum obtainable fluorescence intensity, owing to dissociation in the lowest excited singlet state to the non-fluorescent species.

The relationship between fluorescence radiant flux and analyte concentration (for low analyte concentration) forms the basis of quantitative fluorimetry and is given by:

$$P_{f\lambda'} = 2{\cdot}3\phi_{f\lambda'}P_{0\lambda}\varepsilon_\lambda Cb; \tag{2}$$

where $\phi_{f\lambda'}$ is the quantum yield of fluorescence at the emission wavelength λ'($\phi_{f\lambda'}$ is the spectral quantum yield at λ' times the emission monochromator spectral bandwidth *i.e.*, quantum yield per wavelength interval times the wavelength interval measured), ε_λ is the molar absorptivity at the absorption wavelength λ of the analyte, C is the analyte concentration and b is the pathlength of exciting radiation through the sample. $P_{f\lambda'}$ and $P_{0\lambda}$ are, respectively, the radiant flux of fluorescence falling on the detector at λ' and the radiant flux of exciting radiation incident upon the sample at an absorption wavelength of λ. It is assumed that excitation and emission monochromators are used to select small wavelength intervals at λ' in luminescence. Ordinarily, the product $\phi_{f\lambda'}P_{0\lambda}\varepsilon_\lambda b$ is not evaluated. Rather, the radiant flux of fluorescence of a sample (actually it is usually the signal due to the flux, but the instrumental signal is proportional to the flux reaching the spectrometric system) of known concentration is compared with that of the unknown, according to:

$$\frac{P_{fu\lambda'}}{P_{fs\lambda'}} = \frac{C_u}{C_s}; \tag{3}$$

where $P_{fu\lambda'}$ and $P_{fs\lambda'}$ are the radiant fluxes of fluorescence and C_u and C_s are the analyte concentrations in unknown and standard samples, respectively. Equation (3) is, of course, valid only if $\phi_{f\lambda'}P_{0\lambda}\varepsilon_\lambda b$ is identical for unknown and standard samples—if the analyte is in the same chemical form in the unknown as in the standard sample. The latter condition may not be valid if the analyte has dissociable groups and the pH of the unknown and standard solutions are slightly different—especially if pH $\sim$ pK. Such a situation may arise from simple errors in solution preparation or from absorption of atmospheric carbon dioxide but may be eliminated as a source of error by making the solutions sufficiently acidic or basic so that only one species (the acid or conjugate base) absorbs. Control of instrumental variables can fix $P_{0\lambda}$ and b while for a particular absorbing species at a given wavelength of excitation and temperature and in a given solvent ε_λ is constant. For a fluorescing species not participating in chemical reactions in the electronically excited state, $\phi_{\mathrm{f}\lambda'}$ is a constant at the emission wavelength λ' and in a given solvent at a given temperature.

If the luminescing species contains dissociable groups and the pH of the solution is such that pH $\sim$ pK^*, then $\phi_{\mathrm{f}\lambda'}$ will show a pH dependence[2] given by:

$$\frac{\phi_{\mathrm{f}\lambda'}}{\phi^0_{\mathrm{f}\lambda'}} = (1 - W) + W\left[\frac{(1 + \overleftarrow{k}\tau_0'[\mathrm{H}^+])}{(1 + \overrightarrow{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H}^+])}\right] \tag{4}$$

where $\phi^0_{\lambda\mathrm{f}'}$ is the quantum yield of fluorescence of the excited acid at the emission wavelength λ' when pH $\ll$ pK^*, W is the fraction of excited acid molecules which enter into the equilibrium process in the lowest excited singlet state and is an exponential function of [H$^+$] [(1 − W) is thus the fraction of excited acid molecules which fluoresce without dissociation], $\overrightarrow{k}$ and $\overleftarrow{k}$ are the rate constants for the unimolecular and bimolecular protonation reactions in the excited state, respectively, τ_0 and τ_0' are the mean radiative lifetimes of the excited acid and base, respectively and [H$^+$] is the protonated solvent concentration (in strongly acidic or basic solutions [H$^+$] may be replaced by the Hammett acidity function H_0). If the conjugate base is also fluorescent, the quantum yield of fluorescence $\phi'_{\mathrm{f}\lambda'}$ at the emission wavelength λ' in the region pH $\sim$ pK^*, assuming the acid is excited, will show the pH dependence:

$$\frac{\phi'_{\mathrm{f}\lambda'}}{\phi^{0'}_{\mathrm{f}\lambda'}} = W\left[\frac{\overrightarrow{k}\tau_0}{(1 + \overrightarrow{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H}^+])}\right] \tag{5}$$

where $\phi^{0'}_{\mathrm{f}\lambda'}$ is the quantum yield of fluorescence of the excited conjugate base when pH $\gg$ pK^* and all other symbols have the same meaning as in equation (4). If prototropic equilibrium is essentially complete within the lifetimes of the lowest excited singlet states of acid and conjugate base, then $W \rightarrow 1$, and equations (4) and (5) reduce to:

$$\frac{\phi_{\mathrm{f}\lambda'}}{\phi^0_{\mathrm{f}\lambda'}} = \frac{1 + \overleftarrow{k}\tau_0'[\mathrm{H}^+]}{1 + \overrightarrow{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H}^+]} \tag{6}$$

and

$$\frac{\phi'_{\mathrm{f}\lambda'}}{\phi^{0'}_{\mathrm{f}\lambda'}} = \frac{\overrightarrow{k}\tau_0}{1 + \overrightarrow{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H}^+]}\,. \tag{7}$$

Substitution of equation (4) into equation (2), for an organic acid, yields:

$$P_{\mathrm{f}\lambda'} = P^0_{\mathrm{f}\lambda'}\left[(1 - W) + \frac{W(1 + \overleftarrow{k}\tau_0[\mathrm{H}^+])}{(1 + \overrightarrow{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H}^+])}\right] \tag{8}$$

while for the excited conjugate base formed as a result of excitation of the acid

$$P_{\mathrm{f}\lambda}' = P^{0}_{\mathrm{f}\lambda'}\left[\frac{W\overrightarrow{k}\tau_0}{(1+\overrightarrow{k}\tau_0+\overleftarrow{k}\tau_0'[\mathrm{H}^+])}\right] \tag{9}$$

where $P_{\mathrm{f}\lambda'}$ and $P^{0}{}_{\mathrm{f}\lambda'}$ are the radiant fluxes of fluorescence of the excited acid and its conjugate base, respectively, at the emission wavelengths λ' (however, the emission wavelengths, λ', need not be the same for the acid and base species), and $P\,^{0}_{\mathrm{f}\lambda'} = 2{\cdot}3\,\phi^{0}_{\mathrm{f}\lambda'}P_{0\lambda}\varepsilon_{\lambda}Cb$ and $P^{0'}_{\mathrm{f}\lambda'} = 2{\cdot}3\,\phi^{0'}_{\mathrm{f}\lambda'}P_{0\lambda}\varepsilon_{\lambda}Cb$ are the radiant fluxes of fluorescence of excited acid when pH $\ll$ pK^* and excited base when pH $\gg$ pK^*, respectively. The pH dependence of the total radiant flux of fluorescence $P_{\mathrm{t}\lambda'}$ at the analytical emission wavelength is finally given by the sum of equations (8) and (9):

$$P_{\mathrm{t}\lambda'} = P^{0}_{\mathrm{f}\lambda'}(1-W) + \frac{P^{0}_{\mathrm{f}\lambda'}W(1+\overleftarrow{k}\tau_0'[\mathrm{H}^+]) + P^{0'}_{\mathrm{f}\lambda'}W\overrightarrow{k}\tau_0}{(1+\overrightarrow{k}\tau_0+\overleftarrow{k}\tau_0[\mathrm{H}^+])}. \tag{10}$$

Alternatively, it can be shown that if the ground state of the basic species is excited, the radiant power of fluorescence is

$$P_{\mathrm{t}\lambda'} = P^{0'}_{\mathrm{f}\lambda'}(1-V) + \frac{P^{0}_{\mathrm{f}\lambda'}V(1+\overleftarrow{k}\tau_0'[\mathrm{H}^+]) + P^{0'}_{\mathrm{f}\lambda'}V\overrightarrow{k}\tau_0}{(1+\overrightarrow{k}\tau_0+\overleftarrow{k}\tau_0'[\mathrm{H}^+])}, \tag{11}$$

where V is similar to W but is the fraction of excited base molecules which enter into the equilibrium in the lowest excited singlet state and the ε_{λ} contained in $P^{0}_{\mathrm{f}\lambda'}$ and $P^{0'}_{\mathrm{f}\lambda'}$ is now that of the long wavelength band in the absorption spectrum of the basic species.

The dependence of the radiant flux of fluorescence upon prototropic equilibrium in the lowest excited singlet states of acids and bases can be useful to the analytical chemist. It is possible, by careful adjustment of pH, to determine small amounts of certain substances in the presence of large amounts of interfering substances even though their fluorescence bands strongly overlap, provided that their pK^* values are appreciably different. For example, in the bromination of 8-quinolinol, it is possible to determine[5] the unreacted 8-quinolinol (p$K^* = -6{\cdot}5$) in the presence of the large excess of 5-bromo-8-quinolinol (p$K^* = -7{\cdot}8$), by adjusting the Hammett acidity of the solution to $H_0 = -6$ with perchloric acid so that the 8-quinolinol cation fluoresces while the 5-bromo derivative does not. This selectivity is not possible with absorption spectrophotometry and would not be possible with fluorimetry if it were not feasible to take advantage of the difference in pK^* between these compounds.

On the other hand, the pH dependence of the radiant flux of fluorescence can be a hindrance to the analytical chemist. Adjustment of the pH of the test and standard solutions so that only one species is absorbing the exciting radiation can leave the solutions in a pH region where the radiant flux of luminescence, at the wavelength at which fluorescence is observed, varies appreciably with pH. In this case, the radiant flux of fluorescence may also not be the maximum obtainable, so that some sensitivity may be lost. Even worse, if the standard and unknown solutions are at slightly different pH in the region pH $\sim$ pK^*, the analytical utility of equation (3) will be invalid, owing to the differences in $\phi_{f\lambda'}$ between the standard and unknown solutions. These problems are especially likely to occur in solutions of acids having small values of $\overrightarrow{k\tau_0}$ and bases having small values of $\overleftarrow{k\tau_0}'$, in solutions of high pH, in which case the region of strong pH dependence of $P_{t\lambda'}$ is spread over several pH units. Occasionally, this problem can be eliminated by the obvious method of making the solution sufficiently acidic or basic to be well removed from the pH $\sim$ pK^* region. If this is successful the solution will be in a region where $P_{t\lambda'}$ is not strongly pH-dependent and routine analysis can be performed. However, because pK and pK^* are often different by six or more units, the adjustment of pH to a region where only one species luminesces may leave the solution so strongly acidic or basic that side-reactions may occur (condensation, hydrolysis, rearrangement, *etc*), further complicating analysis.

USE OF THE ISOEMISSIVE POINT FOR ANALYSIS TO MINIMIZE ERRORS DUE TO DISSOCIABLE PROTONS

Analytical problems in fluorimetry, due to the different pH regions in which corresponding ground and excited state equilibria occur, can be minimized for certain acid–conjugate base pairs, provided that both are fluorescent, if an emission wavelength can be found such that $P_{t\lambda'}$ is independent of pH (or [H$^+$]). Such a wavelength is analogous to an isosbestic point in the absorption spectrum of an acid–conjugate base pair, and will hereafter be referred to as an "isoemissive point". Like an isosbestic point, the existence of an isoemissive point is dependent on the presence of only two species derived from the same compound in equilibrium with one another at the pH of the solution. A further stipulation for the existence of an isoemissive point is derived from the invariance of the radiative power of fluorescence with [H$^+$]. Differentiation of equation (10) with respect to [H$^+$] yields

$$\frac{\partial P_{t\lambda'}}{\partial[\mathrm{H}^+]} = \frac{\overrightarrow{k\tau_0}}{(1+\overrightarrow{k\tau_0}+\overleftarrow{k\tau_0}'[\mathrm{H}^+])} \times \left[(P^{0'}_{f\lambda} - P_{f\lambda}{}^{0}) \frac{\partial W}{\partial[\mathrm{H}^+]} + \frac{\overleftarrow{k\tau_0}'}{(1+\overrightarrow{k\tau_0}+\overleftarrow{k\tau_0}'[\mathrm{H}^+])} (P_{f\lambda}{}^{0} - P_{f\lambda}{}^{0'})W \right]. \qquad (12)$$

With the condition that at the isoemissive point $\partial P_{t\lambda'}/\partial[\mathrm{H}^+] = 0$, we get

$$P_{f\lambda}{}^{0'} = P_{f\lambda}{}^{0} \qquad (13)$$

or

$$\phi^{0'}_{f\lambda'} = \phi_{f\lambda}{}^{0}. \qquad (14)$$

Thus the isoemissive point corresponds to that emission (luminescence) wavelength at which the fluorescence quantum yields of excited acid and conjugate base are equal, when only unimolecular deactivating processes are competing with fluorescence and the dissociation process for depopulation of the lowest excited singlet state. Anderson and Weber[6] have observed the occurrence of an isoemissive point in the fluorescence study of the binding of reduced 3-acetylpyridine-adenine dinucleotide by lactic dehydrogenase and have used it to establish that the quantum yields of bound and unbound lactic dehydrogenase were identical *i.e.*, binding did not result in preferential quenching of one form of the enzyme fluorescence.

The fluorescence spectra of 2-naphthol and 1-amino-2-naphthol-4-sulphonic acid at different pH values are shown in Figs. 1 and 2, respectively. These spectra were taken on an Aminco Bowman Spectrophotofluorimeter, with a 150-W xenon lamp as the excitation source and an RCA 1P28 multiplier phototube as the detector. An isoemissive point is clearly discernible for 2-naphthol over the entire pH range while for 1-amino-2-naphthol-4-sulphonic acid an isoemissive point is present in the Hammett range from 0·94 to −1·18. Owing to the polyacidity of the latter compound, more than two species are present in prototropic equilibrium with one another over most of the acidity range, resulting in the absence of isoemissive points at higher and lower Hammett acidity values.

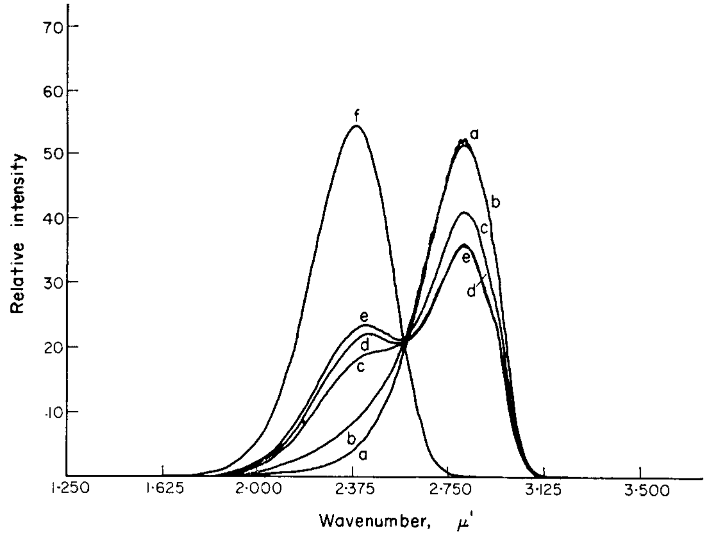

FIG. 1.—Fluorescence spectra of 2-naphthol at several acidities. a—2·30 × $10^{-1}M$ HClO$_4$; b—2·30 × $10^{-2}M$ HClO$_4$; c—2·30 × $10^{-3}M$ HClO$_4$ d—2·30 × $10^{-4}M$ HClO$_4$; e—2·30 × $10^{-5}M$ HClO$_4$; f—1·0 × $10^{-4}M$ NaOH.

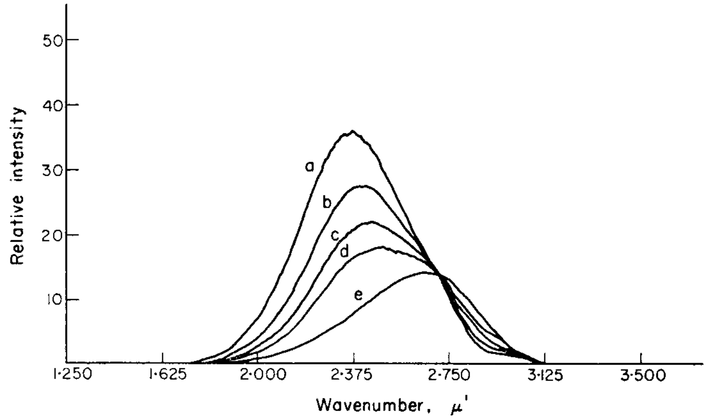

FIG. 2.—Fluorescence spectra of 1-amino-2-naphthol-4-sulphonic acid at several acidities. a—0·115M HClO$_4$; b—0·345M HClO$_4$; c—0·690M HClO$_4$; d—1·15M HClO$_4$; e—2·88M HClO$_4$.

Another possible use of the isoemissive point in analysis is to increase precision of measurement. If an isoemissive point is present, it is possible to use scale expansion techniques to enhance precision by setting the emission wavelength at the isoemissive point. By use of dual emission wavelengths—one wavelength set at the isoemissive point and one wavelength set at some other value—it should also be possible to increase the sensitivity of the measurement.

THE pH DEPENDENCE OF PHOSPHORESCENCE

Because of the differences in electronic repulsions in singlet and triplet states, the electronic dipole moment changes accompanying singlet–triplet transitions are usually much smaller than those accompanying singlet–singlet transitions. As a result, the pK^* values of the lowest triplet states of organic acids and bases are usually much closer to the ground state values than are those of the lowest excited singlet states.[7] From equation (1), it is evident that the frequency shift of the phosphorescence emission of an organic acid or base with changing pH will be generally smaller than that for fluorescence from the same compound.

Owing to the long lifetimes of excited triplet states, collisional deactivation in fluid solution competes seriously with phosphorescence as a mode of depopulation of excited triplet states. Consequently, phosphorescence is almost never observed in fluid solution (solvents at room temperature) and must be studied in rigid glasses (solvents at low temperature, *e.g.*, 77K). In rigid media, the mobility of the solvated proton is very low so that proton exchange between an organic acid and the solvent does not occur appreciably within the lifetime of the excited triplet state. As a result, the excited species in phosphorescence generally corresponds to the ground state species which absorbed the exciting radiation. Thus if the pH of the solution is adjusted prior to freezing, to a region where only one ground state species is present, phosphorescence should be observed from only one species.

The excited species (whether the neutral or dissociated form of an organic acid or the neutral or protonated form of an organic base, the phosphorescence of which is employed for analytical purposes) can frequently make a considerable difference in the intensity of phosphorescence, and hence in the sensitivity of the analysis. The radiant flux of phosphorescence $P_{p\lambda'}$ is given by

$$P_{p\lambda'} = \left[\frac{k_{st}}{k_{st} + k_f + \sum_i k_i}\right] \phi_{p\lambda'} P_{0\lambda} \varepsilon_\lambda C b = k_{st} \tau_f \phi_{p\lambda'} P_{0\lambda} \varepsilon_\lambda C b \tag{15}$$

where $P_{0\lambda}$, ε_λ, C and b have the same significance as in equation (2), k_{st} and k_f are the probabilities of intersystem crossing from the lowest excited singlet state and that of fluorescence, respectively, $\sum_i k_i$ is the total probability of all other first-order and pseudo first-order processes deactivating the lowest excited singlet state, τ_f is the radiative lifetime of the lowest excited singlet state, and $\phi_{p\lambda'}$ is the relative quantum yield of phosphorescence at the emission wavelength λ' and is given by:

$$\phi_{p\lambda'} = \left[\frac{k_p}{k_p + \sum_i k_i'}\right] = k_p \tau_p \tag{16}$$

where k_p is the probability of phosphorescence, $\sum_i k_i'$ is the total probability of all non-radiative first- and pseudo first-order processes deactivating the lowest excited triplet state and τ_p is the radiative lifetime of the lowest excited triplet state.

In general, intense phosphoresence is favoured by large values of k_{st}, k_p, τ_f and τ_p. All processes, other than intersystem crossing, in the lowest excited singlet state decrease the term $k_{st}\tau_f$ in equation (15) and thereby decrease the radiant flux of phosphorescence. Similarly, all processes other than phosphorescence from the lowest excited triplet state decrease $\phi_{p\lambda'}$ and thus the intensity of phosphorescence. The values of k_{st}, k_p, τ_f and τ_p for a phosphorescence are determined by the electronic structure of the molecule as well as its solvent cage and the presence of quenching species in solution.

The inter-relationships between k_{st}, k_p, τ_f and τ_p determine the luminescence flux. For example, aromatic molecules having non-bonded electron pairs on ring heteroatoms (bases) often show the lowest frequency transition in their singlet–singlet absorption spectrum to be of $^1(n \rightarrow \pi^*)$ nature.[8] The $^1(n \rightarrow \pi^*)$ transition is said to be "symmetry-forbidden" [as is the $^1(n \leftarrow \pi^*)$ transition] because of the poor overlap between the non-bonded orbital and the usually orthogonal π^* orbital. As a result, τ_f for an n–π^* lowest excited singlet state is $\sim$100 times greater than that for a π–π^* lowest excited singlet state in the same molecule. Also, the presence of a heteroatom may somewhat enhance spin-orbital coupling in the molecule and result in a greater value of k_{st} than would be encountered in the analogous purely carboxyclic molecule. Consequently, molecules showing low energy $^1(n \rightarrow \pi^*)$ absorptions usually phosphoresce well. If a highly phosphorescent molecule having a non-bonded electron pair is put into a polar solvent, the non-bonded pair may have some σ-bond character induced in it by electrostatic interaction with the positive end of the solvent dipole. In this case, the n–π^* nature of the lowest excited singlet transition may be partially lost so that τ_f decreases and with it the intensity of phosphorescence. If the solution contains acidic species, the non-bonded pair may be completely converted into a σ-bond by co-ordinate covalent bonding (*e.g.*, protonation) in which case the lowest excited singlet state of the molecule will be $^1(\pi$–$\pi^*)$ with an attendant lower value of τ_f and possibly weaker phosphorescence. Examples of the latter phenomena are represented by the fluorescence and phosphorescence of quinoline in polar solvents but only phosphorescence in non-polar ones[9,10] and by the much stronger phosphorescences of the neutral forms of quinoline and acridine than of the protonated forms.[7]

The quenching of the luminescence arising from electronically excited states of aromatic molecules may be due to any of a number of processes occurring between the potential luminescer and the quenching species, *e.g.*, resonance energy transfer and photochemical reaction. There are at least two distinct ways in which pH can affect quenching processes. First, the solvated proton (or hydroxide ion) can react with the phosphorescing species to form the conjugate acid (or base). The conjugate species may be weakly phosphorescent or non-phosphorescent by virtue of its own molecular electronic structure, *i.e.*, the rate of internal conversion in the lowest singlet and/or triplet excited states of the acid may be very different from that in the conjugate base. Table I shows the limits of detection, as determined on the Aminco-Bowman SPF, of the three isomeric mononitrophenols by phosphorimetry, in both neutral and dissociated forms. The neutral form was studied in absolute ethanol containing 1% v/v of 18*M* sulphuric acid, while the dissociated form was studied in absolute ethanol containing 1% v/v of saturated sodium hydroxide solution. The tremendous difference in sensitivity between the neutral and dissociated forms of the *para* isomer is apparent. It is also interesting that the limit of detection of the *p*-nitrophenolate anion is much lower than any of the other species, and that for the *ortho* isomer the limit of detection of the neutral species is actually somewhat lower than that for its conjugate base.

TABLE I.—LIMITS OF DETECTION FOR THE MONONITROPHENOLS AND THEIR ANIONS, BY PHOSPHORIMETRY

p-Nitrophenol		*m*-Nitrophenol		*o*-Nitrophenol	
neutral	anion	neutral	anion	neutral	anion
$1{\cdot}5 \times 10^{-7}M$	$1{\cdot}5 \times 10^{-10}M$	$5{\cdot}2 \times 10^{-8}M$	$6{\cdot}7 \times 10^{-8}M$	$6{\cdot}5 \times 10^{-8}M$	$3{\cdot}0 \times 10^{-7}M$

The second way in which pH affects the quenching of phosphorescence derives from the fact that quenching is a highly specific process. It is possible for the luminescence from a given species to be quenched by some extraneous species and yet the luminescence from the conjugate base (or acid) to be unaffected by the quencher. For example oxygen has a greater tendency to quench some anionic species than their conjugate acids.[11]

For the most part, phosphorimetry has been confined to a few solvent media (EPA*, ethanol, alkyl halides) because of their ability to form clear glasses when frozen. Recently, the ability to use "snowed" solvents[12] has been demonstrated as a result of the development of a rotating sample tube.[13] Thus liquid alkanes are now potential phosphorimetric solvents. However, only the protic solvents (ethanol, EPA, *etc*) allow the advantage of being able to select the prototropic species, derived from the analyte, with the lowest limit of detection, by permitting the variation of pH. Because it is at present impossible to predict accurately, *a priori*, whether the phosphorescence from a neutral species or from its charged conjugate acid or base will be more intense and will therefore yield lower limits of detection, it is prudent to keep in mind that the variation of the pH of the test solution in a protic solvent can be a powerful tool in the analytical application of phosphorescence.[14]

Zusammenfassung—Die Theorie des pH-Einflusses auf Fluoreszenz und Phosphoreszenz organischer Spezies mit Säure-Basen-Eigenschaften wird dargelegt und praktische Anwendungen davon angegeben.

Résumé—On donne un compte-rendu de la théorie de l'influence des variations de pH sur la fluorescence et la phosphorescence d'espèces organiques qui présentent des propriétés acide-base, et des applications pratiques de l'influence.

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* Diethyl ether, isopentane and ethanol; 5:5:2 v/v.

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DETERMINATION OF IRIDIUM IN MAFIC ROCKS BY ATOMIC ABSORPTION*

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Summary—Iridium is determined in mineralized mafic rocks by atomic absorption after fire-assay concentration into a gold bead. Inter-element interferences in the atomic-absorption determination are removed and Ir sensitivity is increased by buffering the solutions with a mixture of copper and sodium sulphates. Substantial amounts of Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Ni, Pb, Te, Ti, V, Y, Zn and platinum metals can be tolerated in the atomic-absorption determination. The sensitivity and detection limits are 3·2 and 0·25 ppm of Ir, respectively.

A MAJOR advance in the atomic-absorption determination of iridium was made by Van Loon[1] who found that the presence of at least 500 ppm of copper and 1000 ppm of sodium in solution minimizes interferences from base and noble metals. Some problems remained, however. For example, we found Van Loon's procedure to be disturbed excessively by sulphate ion and appreciably by variation in the concentration of copper, sodium, and other metals. Furthermore, because no provision was made for the preconcentration of iridium, the procedure is directly applicable only to samples containing iridium as a major constituent.

This paper presents a procedure for the atomic-absorption determination of iridium based on preconcentration of iridium in a gold bead resulting from fire-assay fusion and cupellation. It is directly applicable to mineralized mafic rocks containing at least 2·5 ppm of iridium. To minimize interference and maximize sensitivity, atomic-absorption measurements are made on solutions buffered with copper and sodium sulphates with copper and sodium concentrations maintained at approximately 0·7% and 0·3% respectively. The detection limit (twice the standard deviation) is 0·25 ppm Ir and the sensitivity 3·2 ppm Ir for 1% absorption.

Fire assay is not a generally recommended procedure for the concentration of iridium. For example, Beamish[2] cites losses of as much as 5% in cupellation with silver as a collector, and severe losses to basic or subsilicate slags. We have observed no losses for mafic rocks when sufficient gold is used as a collector and the slag ranges from monosilicate (orthosilicate) to bisilicate (metasilicate) in composition.

EXPERIMENTAL

Reagents and apparatus

Gold wire. For fire-assay, 99·999% pure.

Copper sulphate solution, 7% w/v *copper.* Dissolve 27·5 g of copper sulphate pentahydrate in water and dilute to 100 ml.

Mixed copper–sodium solution. Dissolve 13·75 g of copper sulphate pentahydrate and 4·64 g of sodium sulphate in 50 ml of hydrochloric acid and make up to 100 ml with water.

Standard solutions of iridium. Prepare from ammonium hexachloroiridate a stock solution containing 1·000 mg of iridium per ml in 2% v/v hydrochloric acid. Prepare other solutions by dilution with 2% v/v hydrochloric acid.

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* Publication authorized by the Director, U.S. Geological Survey.

Cylindrical alumina crucibles, 2 ml capacity, for sodium peroxide fusions. Coors AD-999 alumina ceramic crucibles available from Coors Porcelain Company, Golden, Colorado.

Synthetic standards. Two synthetic standards were prepared, using U.S.G.S. dunite DTS-1 as a base. Analyses cited by Flanagan[3] show it to contain negligible amounts of platinum metals. The first standard was made to contain 10 ppm each of Ir and Rh, and the second 10 ppm each of Ir, Os, Pd, Pt, Rh and Ru. Iridium contents were verified by activation analysis while Pd, Pt and Rh contents were verified by fire-assay/atomic-absorption procedures.[4,5] The fate of Os and Ru was not ascertained. The standards are prepared as follows. To weighed samples of dunite finer than 200 mesh in porcelain casseroles, add water to form a slurry. Add the required amounts of standard solutions of the appropriate platinum metals and mix. Evaporate the solutions on a steam-bath, stirring the slurries frequently. Dry the residues in an oven at 110° and then heat in a furnace at 450° for approximately 30 min. Roll the samples in a ceramic jar mill with alumina balls for 3 hours. Mix and bottle.

Instrument parameters and settings

A Perkin–Elmer Intensitron hollow-cathode tube with a Perkin–Elmer Model 303 instrument was used in the experiments. The conditions were as follows.

Wavelength	263·97 nm
Slit	0·3 mm
Hollow-cathode current	30 mA
Fuel, acetylene pressure	69 kN/m^2 (10 psi)
flow-meter setting	8·5
Oxidizer, air pressure	190 kN/m^2 (28 psi)
flow-meter setting	7·5
Flame	oxidizing
Burner	standard head
Aspirator	adjusted for uptake of ∼3 ml/min

Conditions for other instruments must be found by trial and error.

Procedure

The fire-assay fusion and cupellation procedures used here follow generally accepted practices as described by Bugbee.[6] A bisilicate slag composition is to be preferred. For a 20-g sample of dunite, a flux consisting of 50 g of lead (II) oxide, 35 g of sodium carbonate, 15 g of silica, 19 g of sodium tetraborate and 4 g of flour will yield both a satisfactory lead button and a bisilicate slag. The fusion is made in the presence of 50 mg of added gold for the quantitative collection of Ir, Pd, Pt, and Rh.

Transfer the gold bead obtained on cupellation to a small beaker. Add 5 ml of *aqua regia*, cover and allow the mixture to react at room temperature for approximately 1 hr. Heat on a steam-bath for several hr more. Add 3 ml of water and a small amount of paper pulp, mix and filter through a 42·5-mm medium porosity filter paper. Wash the iridium residue with water. Reserve the filtrate for the determination of Pd, Pt, and Rh. Ignite the residue in a 2-ml alumina crucible at 600° starting with a cold furnace. Add 100 ± 10 mg of sodium peroxide by calibrated dipper and carefully fuse the residue. Heat for 5 min more, maintaining in the molten state. Cool. Add 1·5 ml of water, cover and allow to stand at room temperature for approximately 15 min. Warm the mixture until the melt disintegrates, and transfer the solution to a 25-ml beaker by several alternating washes with 1-ml portions of concentrated hydrochloric acid, nitric acid and water. Add 0·15 ml of sulphuric acid (1 + 1) by pipette to convert sodium salts into sulphate and evaporate the solution on a steam-bath. Add 2 ml of hydrochloric acid (1 + 1), warm briefly to dissolve salts and transfer the solution to a 10-ml volumetric flask with water. Dilute to volume with water and mix. Transfer a 5-ml aliquot of the solution to another 10-ml volumetric flask, and reserve the remainder for the determination of Pd, Pt and Rh. Add 1 ml of hydrochloric acid (1 + 1) and 1 ml of copper sulphate solution. Adjust to volume with water and mix. Prepare iridium standards and a blank, each containing 1 ml of mixed copper-sodium solution in a 5-ml volume. Determine iridium in all solutions by atomic absorption.

RESULTS

Buffering agents

The interference of sulphate in Van Loon's procedure has been noted in the introduction. For example, the absorbance of 200 ppm of iridium in a solution also containing 500 ppm of copper and 1000 ppm of sodium as chlorides increases approximately 10 and 40% in the presence of 10 and 100 ppm of sulphate respectively.

Similarly, when the sulphates of sodium and copper are substituted, maintaining the same metal concentrations, the absorbance of 200 ppm of iridium increases approximately 200%. From these results a sulphate system would seem to be advantageous.

The potential of various sulphates for minimizing interference of other noble metals was determined on test solutions containing 200 ppm of Ir and from 100 to 500 ppm each of the various noble metals. Of the many salts tried, copper, sodium and cadmium sulphates individually or together in binary and ternary mixtures all showed excellent reduction of interference. While a given salt or salt mixture would prove superior in the reduction of interference of a specific noble metal, best results for all noble metals were obtained with a mixture of 7 parts of copper and 3 parts of sodium at a total metal concentration of 10000 ppm. These conditions were adopted.

The greater effectiveness of the 7:3 copper–sodium mixture over that of sodium or copper alone in overcoming the depressive interference of 300 ppm of rhodium on 200 ppm of iridium is illustrated in Fig. 1. It is also apparent that the copper-sodium sulphate system is insensitive to changes in total metal concentration as long as the final total metal concentration is in the range 0·75–1·5%.

Figure 2 shows that a concentration of 500 ppm of rhodium produces a 5% relative error in the determination of 200 ppm of iridium. The magnitude of this error is independent of the weight ratio of copper to sodium in the range 1·5–4.

Effect of hydrochloric acid concentration

The absorbance of iridium decreases approximately 4% for each 10% by volume increase of hydrochloric acid concentration. A 10% v/v hydrochloric acid concentration was adopted.

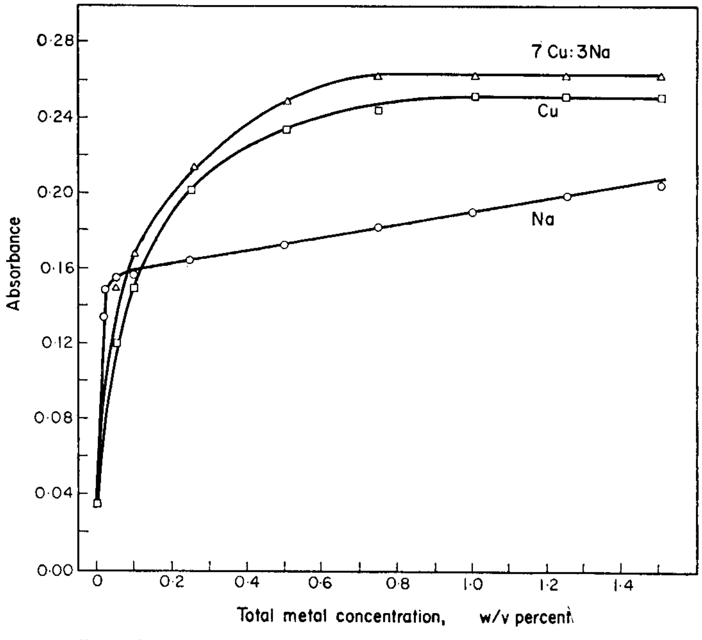

FIG. 1.—Effect of concentration of various sulphates on the absorbance of 200 ppm of Ir in the presence of 300 ppm of Rh in 10% v/v hydrochloric acid.

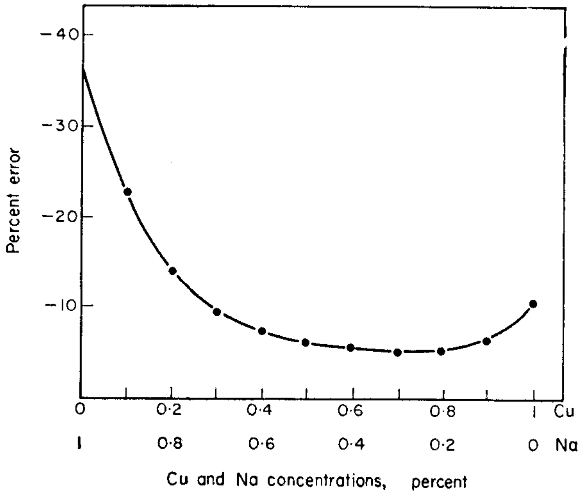

FIG. 2.—Errors in the absorbance of 200 ppm of Ir caused by 500 ppm of Rh, as a function of copper–sodium ratio.

Tolerances for other elements

In atomic-absorption determination of 20 or 200 ppm of iridium, the copper–sodium system tolerates separately (error less than 2 %) 1000 ppm each of Al, Bi, Ca, Cd, Co, Cr, Fe, Hg, Ho, K, La, Mg, Mn, Mo, Ni, Pb, V, Y or Zn, 500 ppm each of Au, Pd, Pt, Os and Ru and 20 ppm of Ag, the maximum amount of each element tested. Rhodium should be restricted to 300 ppm. At the 20-ppm level of iridium 1000 ppm each of Te and Ti do not interfere, but only half these concentrations can be tolerated at 200 ppm of iridium. No interference was observed in the determination of 20 or 200 ppm of iridium in solutions also containing mixtures of 200 ppm each of Au, Pd, Pt, Os, Rh and Ru. When the total procedure is considered, substantially larger amounts of these elements can be tolerated inasmuch as they are largely separated from iridium during the dissolution of the gold bead following cupellation.

Standard curve

A plot of net absorbance *vs.* iridium concentration at 264 nm yields a straight line up to a concentration of 200 ppm of iridium, the maximum tested. The sensitivity is 3·2 ppm of Ir for 1 % net absorption. The detection limit (at twice the standard deviation) is 0·25 ppm.

The fire assay

With 20-g samples of each of the prepared iridium-dunite standards, at least 95 % of the iridium was collected when 30 mg or more of gold were used as a carrier in the cupellation. With 10 mg of gold, iridium recoveries averaged only 87 %. A 50-mg gold bead was adopted for the recommended procedure. It was also observed that a single fire-assay fusion sufficed for the quantitative recovery of Ir, Pd, Pt and Rh, with slags varying from monosilicate to bisilicate in composition.

In the parting of the gold bead with *aqua regia*, iridium was invariably completely insoluble while gold, palladium and platinum were completely soluble. The fate of rhodium depended on the amount of gold used. With 50 mg of gold approximately 91 % of the rhodium dissolved; with 30 mg of gold 73 % of the rhodium was soluble, and with 10 mg of gold only 40 % of the rhodium dissolved.

Test of total procedure

Fifteen dunite standards containing 10 ppm each of Ir and Rh and fifteen containing 10 ppm each of all six platinum metals were taken through the total procedure. Inasmuch as the results obtained on each set did not differ significantly, all results were lumped together. The average recovery of iridium was found to be 98·2 % with a standard deviation of 2·1 %, assuming the iridium content of the samples to be exactly 10 ppm. The overall average obtained on 8 samples by Paul Greenland of this laboratory by triple coincidence counting of ^{192}Ir after neutron activation amounted to 10·2 ppm with a standard deviation of 0·5 ppm.

To exclude the possibility that the other platinum metals in the samples were necessary carriers for Ir during the fire assay, four 20-g samples of dunite containing 10 ppm of iridium alone were also processed. No significant differences were found in the recovery of iridium from these and the previous samples. Finally there remained the question of how small an amount of iridium can be determined without loss in the procedure. Accordingly 20-g samples salted to contain from 50 to 200 μg of Ir were taken for analysis. Again no noticeable differences in recoveries were obtained. Thus the procedure should be applicable to samples containing as little as 2·5 ppm of Ir.

Zusammenfassung—Iridium wird in mineralisierten Magnesium-Eisen-Gesteinen nach Schmelzanreicherung in der Goldperle durch Atomabsorption bestimmt. Durch Puffern der Lösungen mit einer Mischung von Natrium- und Kupfersulfat werden gegenseitige Störungen der Elemente beseitigt und die Iridium-Empfindlichkeit erhöht. Die Anwesenheit erheblicher Mengen Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Ni, Pb, Te, Ti, V, Y, Zn und der Platinmetalle ist bei der Atomabsorptionsbestimmung zulässig. Empfindlichkeit und Nachweisgrenze betragen 3,2 bzw. 0,25 ppm Ir.

Résumé—On dose l'iridium dans les roches "mafiques" (d'origine ferromagnésienne) minéralisées par absorption atomique après concentration par voie sèche dans une perle d'or. Les interférences inter-éléments dans le dosage par absorption atomique sont éliminées et la sensibilité pour Ir est accrue en tamponnant les solutions avec un mélange de sulfates de cuivre et de sodium. Des quantités importantes de Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Ni, Pb, Te, Ti, V, Y, Zn et métaux du platine peuvent être tolérées dans la détermination par absorption atomique. Les limites de sensibilité et de détection sont de 3,2 et 0,25 ppm d'Ir, respectivement.

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STUDIES ON NUCLEATION FROM SOLUTION OF SOME ANALYTICALLY IMPORTANT METAL CHELATES

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Summary—The combination of precipitation from homogeneous solution and Vonnegut's droplet technique is employed in the study of nucleation from solution of bis(1,2-cyclohexanedionedioximato)-Ni(II), bis(1,2-cycloheptanedionedioximato)Ni(II), bis(1,2-cyclohexanedionedioximato)Pd(II) and bis(1,2-cycloheptanedionedioximato)-Pd(II). Values of the kinetic constant, surface energy, critical radius and the number of molecules per critical nucleus are calculated and discussed in terms of the limitations of the classical theory of nucleation when applied to crystal nucleation from aqueous solutions of electrolytes.

IN PREVIOUS communications[1,2] it was suggested that a combination of precipitation from homogeneous solution[3] and Vonnegut's droplet technique[4] could be used to study homogeneous nucleation from solution. This combination utilizes both the controlled build-up of supersaturation and the sequestering of motes within the system, the respective advantages offered by the two techniques. Consequently, the data required for investigation of the nucleation of compounds of interest, namely the rate of homogeneous nucleation as a function of the supersaturation attained by the system, can be obtained experimentally.

The purpose of this communication is to report and discuss the results of nucleation studies on four analytically important metal chelates: bis(1,2-cyclohexanedionedioximato)nickel(II), bis(1,2-cycloheptanedionedioximato)nickel(II), bis(1,2-cyclohexanedionedioximato)palladium(II) and bis(1,2-cycloheptanedionedioximato)palladium(II).

EXPERIMENTAL

The reaction between a suitable α-diketone and hydroxylamine in the presence of the metal ion of interest was used to generate, *in situ*, the metal chelate under study. Aqueous solutions containing the reactants were dispersed in light mineral oil and then photomicrographs were taken to record the result of crystal nucleation within the droplets.

Apparatus

The dispersions were prepared with the aid of a microhomogenizer, then placed in cups (diameter 32 mm, height 25 mm) made from Nessler tubes, and were then centrifuged.

The droplets were examined with a polarizing microscope (crossed polarizers, 40× magnification) provided with high intensity illumination from a 600-W projector lamp.

The photographs were taken with a microscope camera at a shutter speed of 0·5 sec. The 35-mm slides were projected onto a calibrated screen so that accurate drop diameter measurements could be made.

Procedure

A typical nucleation study involved three separate experiments: a droplet experiment, a kinetic experiment and a solubility determination. Immediately before a droplet experiment on a given system, two stock solutions were prepared for that system. The two stock solutions were mixed so as to yield the optimum solution conditions for the nucleation study (see Table I). After mixing, a

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small drop (0·01–0·02 ml) of the reaction solution was added to 6 ml of light mineral oil contained in a micro-homogenizer flask and stirred for 15 sec at about 15000 rpm. The resulting dispersion was transferred to a Nessler cup and centrifuged for 15 sec. Then the main part of the dispersion was decanted. The part remaining in the cup was centrifuged again for 30 sec. Photomicrographs of the dispersion were taken at 30-sec intervals.

The kinetic experiment was carried out by mixing the stock solutions in the same proportions used for the droplet experiment and then determining the weight of precipitate formed per unit volume, as a function of time.

In order to determine the solubility of the metal chelate, a medium containing all the components of the reaction solution, except the metal ion and the diketone (see Table I) was saturated with the chelate. After equilibration, organic matter in the solution was destroyed by wet-ashing. The concentration of the metal ion in solution was determined by EDTA titration.[5,6]

TABLE I.—INITIAL SOLUTION CONDITIONS FOR THE NUCLEATION STUDIES

System	M^{+2}, [*M*]	HCl, [*M*]	$NH_2OH \cdot HCl$, [*M*]	α-Diketone, [*M*]
$Ni(C_6H_9N_2O_2)_2$*	0·2	0·03	1	0·4
$Ni(C_7H_{11}N_2O_2)_2$†	0·1	—	0·2	0·2
$Pd(C_6H_9N_2O_2)_2$	0·1	1	0·7	0·2
$Pd(C_7H_{11}N_2O_2)_2$	0·03	6	0·2	0·3

Added conditions:
* Urea (2*M*).
† Phosphoric acid (0·3*M*) ammonium acetate (0·4*M*).

RESULTS

From the photomicrographs, the number and diameters of the droplets containing one crystal were recorded as a function of the lapsed time between mixing of the reagents and the appearance of a crystal within the droplet. An analysis of the data indicated that there was a correlation between the median crystallization time and the logarithm of the droplet diameter. Figure 1 shows the correlation. This was used to

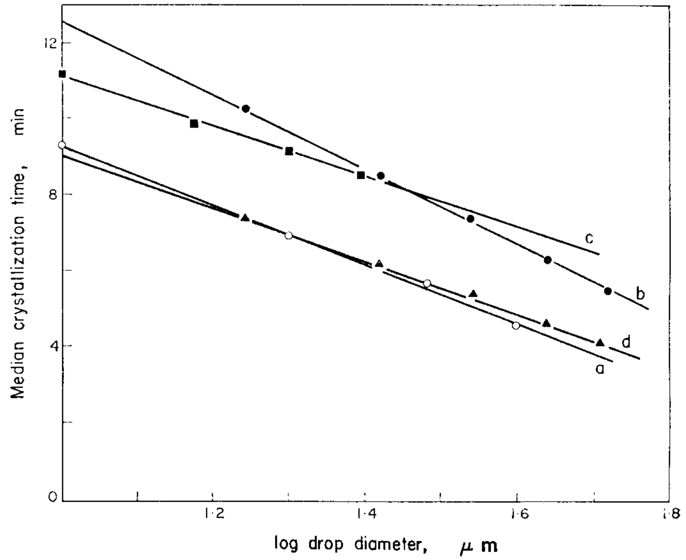
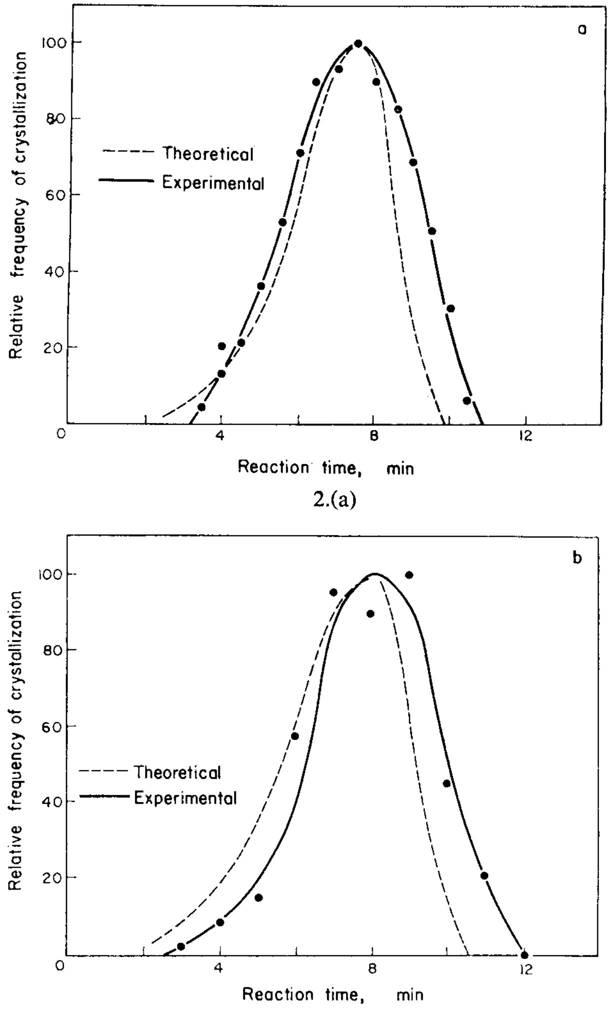


FIG. 1.—Median crystallization time *vs.* log drop diameter for the Ni(II) and Pd(II) chelates. *a*, $Ni(C_6H_9N_2O_2)_2$; *b*, $Ni(C_7H_{11}N_2O_2)_2$; *c*, $Pd(C_6H_9N_2O_2)_2$; *d*, $Pd(C_7H_{11}N_2O_2)_2$.

reduce the crystallization time of any droplet to that of a standard sized droplet. The results of these calculations are presented in Fig. 2 as plots of the relative frequency of crystallization of a standard droplet *vs.* crystallization time.

The probability of crystallization within a standard droplet as a function of crystallization time was calculated from the plots shown in Fig. 2. The results are shown as the solid lines of Fig. 3.

The dependence of the rate of nucleation, J, on the supersaturation, S, of the solute within the droplets was calculated from the slopes[7] of the curves shown in Fig. 3,

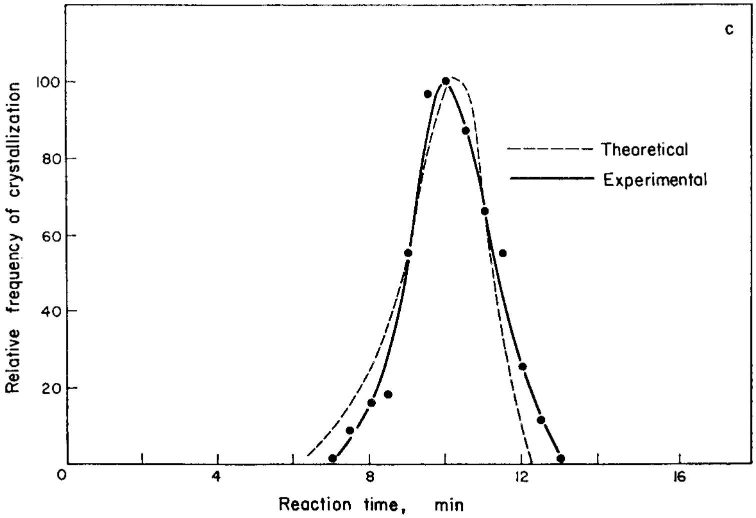


2.(a)

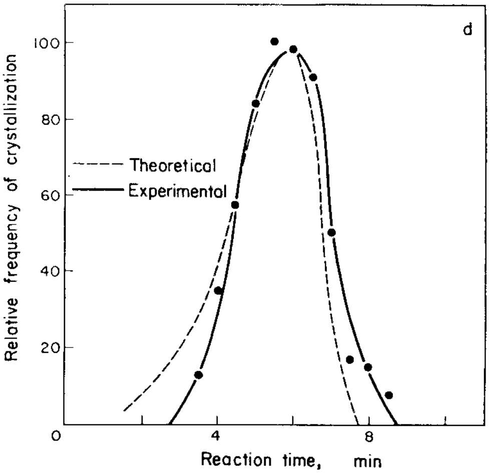
2.(b)

FIG. 2.—Relative frequency of crystallization *vs.* reaction time for the Ni(II) and Pd(II) chelates.

Compound	Standard droplet diameter μm
a $Ni(C_6H_9N_2O_2)_2$	20
b $Ni(C_7H_{11}N_2O_2)_2$	35
c $Pd(C_6H_9N_2O_2)_2$	15
d $Pd(C_7H_{11}N_2O_2)_2$	35



2.(c)



2.(d)

combined with the results of the kinetic experiments shown in Fig. 4. The results of these calculations are shown in Fig. 5.

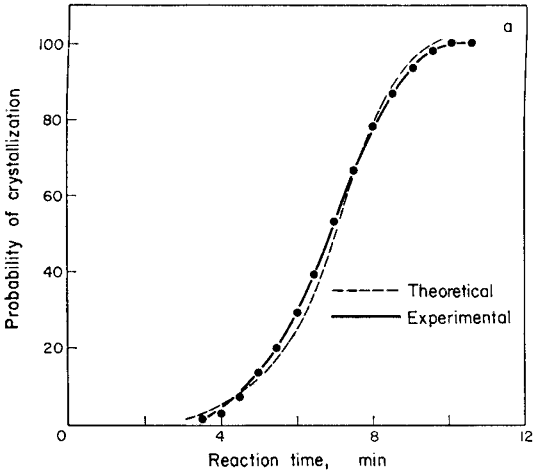
The kinetic constant, A, of the classical nucleation rate equation[8] for each chelate studied was evaluated from the intercepts of the curves in Fig. 5. These are collected in Table II. Various other parameters of importance in classical nucleation theory were calculated[9] from the values of J and S at the point of maximum crystallization frequency. Table II also shows these results for each of the chelates.

DISCUSSION AND CONCLUSIONS

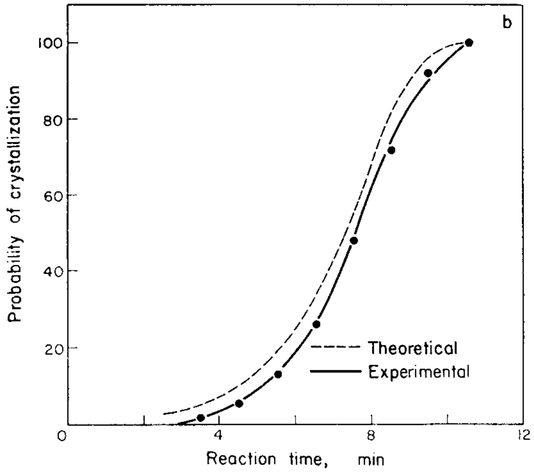
A linear relationship between the median freezing temperature and the logarithm of the droplet diameter was observed by Bigg[11] in his studies on the supercooling of water droplets. To interpret his data, Bigg derived a relationship between freezing temperature, droplet volume and duration of supercooling. Equation (1), analogous to Bigg's equation, has been used to interpret the data found in the present studies.

$$\ln(1 - P) = -\int_0^t Vf(S)\,dt \tag{1}$$

where P = probability of crystallization, t = crystallization time, V = droplet volume, $f(S)$ = some function of the supersaturation.



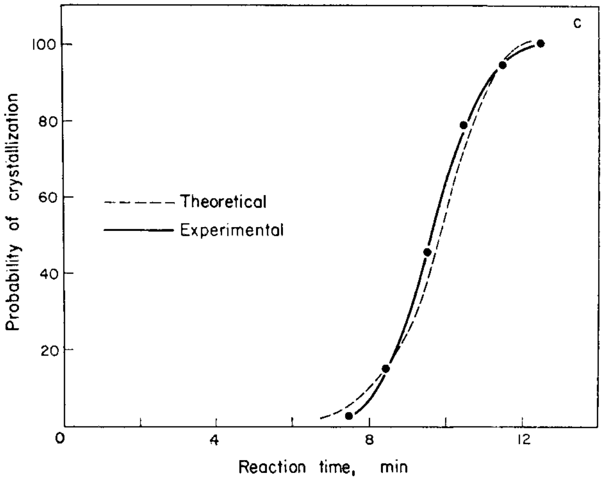
3.(a)



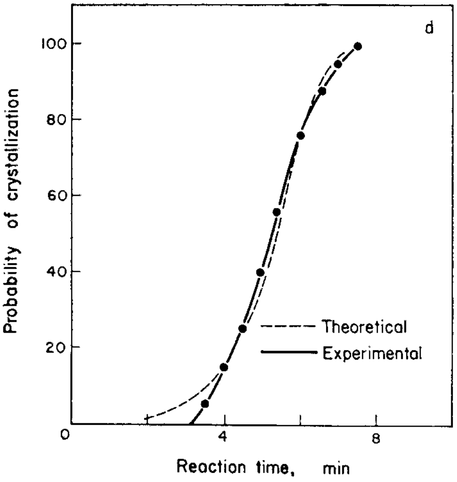
3.(b)

FIG. 3.—Probability of crystallization *vs.* reaction time for the Ni(II) and Pd(II) chelates.

Compound	Standard droplet diameter μm
a $Ni(C_6H_9N_2O_2)_2$	20
b $Ni(C_7H_{11}N_2O_2)_2$	35
c $Pd(C_6H_9N_2O_2)_2$	15
d $Pd(C_7H_{11}N_2O_2)_2$	35



3.(c)



3.(d)

In order to apply equation (1), it was necessary to transform the relationships of Fig. 1 from

$$\bar{t} = m \log d + c \tag{2}$$

into

$$\ln V = a\bar{t} + b \tag{3}$$

where $a = 6{\cdot}9/m$, and $b = -(6{\cdot}9c/m + 0{\cdot}65)$, m = slope from Fig. 1, c = intercept from Fig. 1, $\bar{t}$ = median crystallization time, d = droplet diameter.

At any given time, t, during a droplet experiment there will be a certain droplet volume for which $P = 0{\cdot}5$. From this and equations (1) and (3), it follows that

$$\int_0^t f(S)\,\mathrm{d}t = 0{\cdot}693 \exp(-b)\,[\exp(-at) - 1]. \tag{4}$$

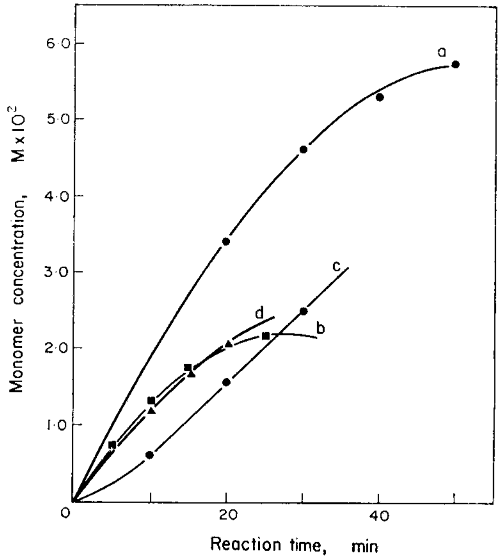


FIG. 4.—Monomer concentration *vs.* reaction time for the Ni(II) and Pd(II) chelates *a*, $Ni(C_6H_9N_2O_2)_2$; *b*, $Ni(C_7H_{11}N_2O_2)_2$; *c*, $Pd(C_6H_9N_2O_2)_2$; *d*, $Pd(C_7H_{11}N_2O_2)_2$.

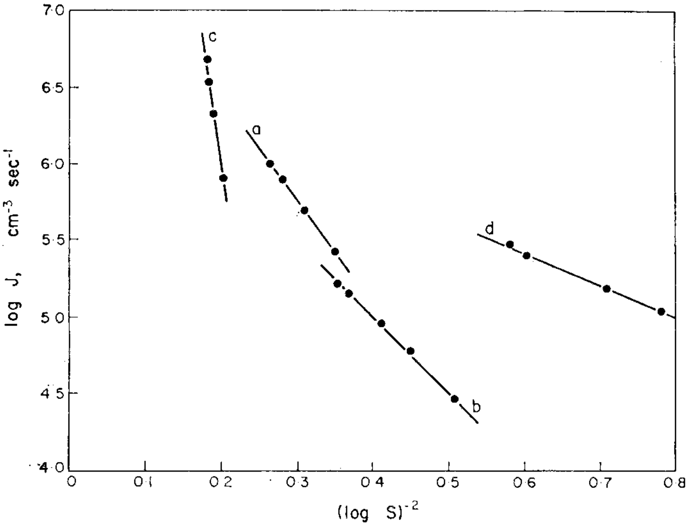


FIG. 5.—Log *J* *vs.* (Log $S)^{-2}$ for the Ni(II) and Pd(II) chelates *a*, $Ni(C_6H_9N_2O_2)_2$; *b*, $Ni(C_7H_{11}N_2O_2)_2$; *c*, $Pd(C_6H_9N_2O_2)_2$; *d*, $Pd(C_7H_{11}N_2O_2)_2$.

Further, at any given time the value of $\int_0^t f(S)\,\mathrm{d}t$ is the same for all droplets. Consequently, equations (1) and (4) can be used to calculate the value of P for droplets of any standard size, V_s. The results of such calculations are shown as broken lines on Fig. 3. Since $(\partial P/\partial t)V_s$ is proportional to the crystallization frequency, equation (5) was used to calculate the frequency as a function of time.

$$-\left(\frac{\partial P}{\partial t}\right) = K \exp(-at)(1-P) \tag{5}$$

TABLE II.—VALUES OF VARIOUS NUCLEATION PARAMETERS FOR THE Ni(II) AND Pd(II) CHELATES

Compound	Solubility M	A $cm^{-3} \cdot sec^{-1}$	S	Surface energy, $erg \cdot cm^{-2}$ (σ)	Critical radius Å (r^*)	Molecules/ nucleus (n^*)
$Ni(C_6H_9N_2O_2)_2$	$1{\cdot}7 \times 10^{-4}$	1×10^8	88	34	12	25
$Ni(C_7H_{11}N_2O_2)_2$	$2{\cdot}4 \times 10^{-4}$	2×10^2	49	29	14	30
$Pd(C_6H_9N_2O_2)_2$	$2{\cdot}3 \times 10^{-5}$	1×10^{12}	$2{\cdot}5 \times 10^2$	36	12	19
Pd $(C_7H_{11}N_2O_2)$	$3{\cdot}5 \times 10^{-4}$	5×10^6	21	23	16	38

* See Table I for solution conditions. The non-S.I. units previously used have been retained to facilitate comparison. In a short communication[10] on the nucleation of $Pd(C_6H_9N_2O_2)_2$, the values given for S, σ and r^* were different from the present values. The values above are based on improved methods of analysis.

where $K = [aV_s]\,[0{\cdot}693 \exp(-b)]$. The results are shown as broken lines on Fig. 2. The discrepancy between the experimental and calculated curves of Figs. 2 and 3 is thought to be due to experimental error.

The usual value[12,13] of the kinetic constant, A, computed by Turnbull and Vonnegut[14] for the homogeneous nucleation of crystals from melts, was used to calculate the various nucleation parameters shown in Table II. The experimental values of A, however, were found to differ by many orders of magnitude from 10^{30} cm^{-3}. sec^{-1} (see Table II). This may be attributed partially to the large entropy changes which accompany crystallization of compounds of some structural complexity, *i.e.*, the activation of the molecules for interface transfer must be accompanied by a large entropy decrease. As Dunning[15,16] points out, the entropy change which occurs during phase transformations is neglected in the Becker-Döring theory. Similar discrepancies between the theoretical and experimental values of A have been reported[8,15,16] and discussed[15,16] previously by other investigators.

Another explanation for the discrepancy between the observed and calculated values of the kinetic constant can also be found in the classical theory. The validity of the functional relationships predicted by equation (6) when applied to nucleation of liquid drops from the vapour is being debated at the present time.[17,18]

$$J = A \exp\left(-\frac{16\pi\, v^2\, \sigma^3}{3(kT)^3\,(2{\cdot}303 \log S)^2}\right) \tag{6}$$

where k = Boltzmann's constant, T = absolute temperature. With the added complication of the ionic nature of the species present in solutions of electrolytes and the significant solvation and entropy effects which are known to accompany nucleation in such solutions, it is doubtful if agreement between predicted and calculated values of A should be expected.

Acknowledgement—The authors acknowledge the financial assistance provided by the National Research Council of Canada and the Department of University Affairs, Province of Ontario, Canada.

Zusammenfassung—Die Kombination der Fällung aus homogener Lösung und der Tröpfchenmethode nach Vonnegut wurde bei der Untersuchung der Keimbildung aus Lösungen von Bis(1,2-cyclohexandiondioximato)Ni(II), Bis(1,2-cycloheptandiondioximato)-Ni(II), Bis(1,2-cyclohexandiondioximato)Pd(II) und Bis(1,2-cycloheptandiondioximato)Pd(II) verwendet. Werte für die kinetische Konstante, die

Oberflächenenergie, für den kritischen Radius und die Anzahl von Molekülen pro kritischem Keim werden berechnet und diskutiert im Hinblick auf die Grenzen der klassischen Keimbildungstheorie bei der Anwendung auf Kristallkeimbildung aus wäßrigen Elektrolytzlösungen.

Résumé—On emploie la combinaison de la précipitation à partir d'une solution homogène et de la technique de gouttelette de Vonnegut dans l'étude de la nucléation à partir d'une solution de bis(1,2-cyclohexanedione dioxamato) Ni(II), bis(1,2-cycloheptanedione dioxamato) Ni(II), bis(1,2-cyclohexanedione dioxamato) Pd(II) et bis(1,2-cycloheptanedione dioxamato) Pd(II). On calcule les valeurs de la constante cinétique, de l'énergie de surface, du rayon critique, et le nombre de molécules par noyau critique et en discute par rapport aux limitations de la théorie classique d'amorçage lorsqu'on l'applique à l'amosçage du cristal à partir de solutions aqueuses d'électrolytes.

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SHORT COMMUNICATIONS

Determination of carbon monoxide in metal carbonyl complexes—II Development of a volumetric finish

(*Received* 4 *December* 1969. *Accepted* 17 *December* 1969)

IN AN EARLIER paper[1] a method was described for the determination of carbon monoxide in metal carbonyl complexes. Carbon monoxide is displaced from the complex by an oxidative technique and oxidized by the Schütze reagent to carbon dioxide which is determined gravimetrically by absorption on soda asbestos in a conventional Pregl-type absorption tube. A modification is now described in which the carbon monoxide is estimated titrimetrically. This is more suitable for normal laboratory conditions and avoids the stringent analytical conditions required for an accurate gravimetric finish. It also permits the use of a smaller sample size without loss in accuracy.

The recommended titrimetric procedure utilizes the method adopted by Unterzaucher[2] for the determination of oxygen in organic compounds. The carbon monoxide is displaced as before by an oxidative procedure and reacted with anhydro-iodic acid at 120°. Iodine, which is quantitatively released at this temperature, is absorbed in aqueous sodium hydroxide and estimated by the six-fold amplification technique of Leipert as modified by Fildes and Macdonald.[3]

EXPERIMENTAL

Apparatus

The apparatus described in the previous publication has been modified (see Fig. 1) to permit the use of anhydro-iodic acid at 120°. The decomposition and purification sections *A–F* as previously described are retained.[1] The new oxidation tube *G* of 12 mm bore is 0·25 m long. It contains a 100-mm section of anhydro-iodic acid *H*, held in place by 3-mm pads of glass-wool and heated to 120° by the furnace *I* (Hösli electrical furnace operated from a 36-V constant voltage transformer). A ball joint connects the oxidation tube to the absorption tube *J* of 12 mm bore. This 0·25-m long tube has indentations along about 0·15 m of its length and the end near the ball joint is heated by the 50-mm long aluminium heating block *K*. A glass tube insert of 7 mm outside diameter and 70 mm length, held in the oxidation tube by a tightly fitting O-ring, ensures that iodine sublimes well into the absorption tube, avoiding loss through the ball joint. The gas flow may be checked by a flow-meter *L* connected to the exit end of the absorption tube.

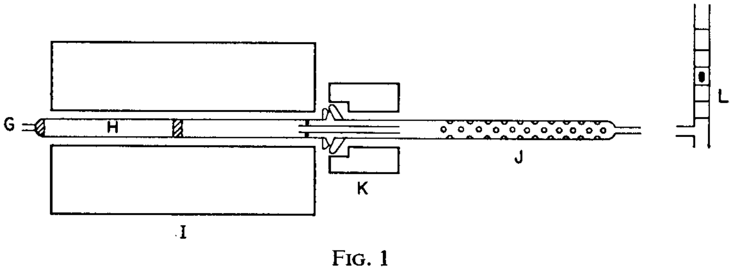

FIG. 1

Reagents

The following reagents are necessary in addition to those previously listed.

Anhydro-iodic acid. Prepared according to the method of Unterzaucher.[4] It is essential that this reagent be prepared and stored in subdued light. The product must remain white at the operating temperature.

Sodium hydroxide, 5*M* and 1*M*.

Phosphoric acid, 3*M*.

Bromine water. Saturated aqueous solution.

Formic acid, 90%. Analytical reagent grade.

Method

Assemble the apparatus and tube packings as described. Adjust the sample flask heating block to 60–70°, the oxidation tube furnace to 120°, the absorption tube heating block K to about 120° and the nitrogen carrier-gas flow to 5–10 ml/min. Allow the nitrogen carrier-gas to purge the apparatus for at least 12 hr and then activate the anhydro-iodic acid by decomposing about 10 mg of sodium formate in the sample flask. Cool the condenser with tap water and immerse the cold trap in solid carbon dioxide and acetone.

To charge the absorber draw $5M$ sodium hydroxide into the tube and allow the reagent to drain. Weigh the sample (3–5 mg) into the reaction vessel, add about 30–50 mg of pyridine hydrobromide perbromide and immediately connect the flask to the apparatus. Add 3 ml of dichloromethane from the dropping funnel B under nitrogen flow and continue the nitrogen flow at 5–10 ml/min while the flask is heated to 70° for about 20 min. Disconnect the absorption tube and rinse the contents into a 250-ml conical flask with distilled water followed by 4 ml of $1M$ sodium hydroxide and further distilled water. Acidify the resulting solution by the addition of 2 ml of $3M$ phosphoric acid, add 5 ml of bromine water, and set aside for 5 min. Destroy the free bromine by the dropwise addition of formic acid and after cooling the solution for 15 min in ice water add 2 ml of $4M$ sulphuric acid and a few crystals (about 50 mg) of potassium iodide. Titrate the liberated iodine with $0{\cdot}02M$ sodium thiosulphate.

$$1 \text{ ml of } 0{\cdot}02M \text{ sodium thiosulphate} \equiv 0{\cdot}2334 \text{ mg of CO.}$$

RESULTS AND DISCUSSION

The results obtained for a range of compounds are given in Table I. These compounds, which were either available commercially or obtained from research projects, all give satisfactory analytical figures for carbon on combustion analysis. It is apparent that an acceptable order of accuracy has been retained with a 3–5-mg sample, which is smaller than that previously recommended.

TABLE I.—DETERMINATION OF CARBON MONOXIDE IN METAL CARBONYL COMPLEXES

Sample*	Carbon monoxide, %	
	Theory	Found
$Mo(CO)_3(P\phi_3)_2Cl_2$	10·81	10·8
$Mo(CO)_4$·phen	28·87	28·9
$Mo(CO)_6$	63·63	64·0
$W(CO)_6$	47·73	48·3
$W(CO)_3$·phen·I_2	11·97	11·6
$[Co(CO)_4CF_2]_2$	50·68	50·7
$W(CO)_3(As\phi_3)_2I_2$	7·41	7·2
$W(CO)_3(Sb\phi_3)_2Br_2$	9·31	8·5
$W(CO)_3(Sb\phi_3)_2I_2$	6·85	6·4

* $\phi = C_6H_5$; phen = 1,10-phenanthroline.

The main difficulty with this modification concerns the quality and reactivity of the anhydro-iodic acid reagent. We find that the reagent functions satisfactorily provided it is prepared strictly in accordance with the conditions set down by Unterzaucher,[4] and that the temperature of the reagent in the furnace is not allowed to rise above 120°. (Higher temperatures up to 135° were found to cause decomposition of this reagent, resulting in high blanks.) All of four batches prepared were active for the oxidation of carbon monoxide to carbon dioxide, and give blank values around 0·03–0·05 ml of $0{\cdot}02M$ sodium thiosulphate. In our experience, commercially available iodine pentoxide is quite unreliable for this oxidation, although it has been reported that iodine pentoxide is more active in oxidizing carbon monoxide than is anhydro-iodic acid.[5]

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Summary—The method previously described for the determination of carbon monoxide in metal carbonyl complexes has been modified to provide an accurate volumetric finish.

Zusammenfassung—Die früher beschriebene Methode zur Bestimmung von Kohlenmonoxid in Metallcarbonylkomplexen wurde abgeändert und bietet jetzt einen genauen volumetrischen Abschluß.

Résumé—La méthode antérieurement décrite pour le dosage de l'oxyde de carbone dans les complexes métal-carbonyle a été modifiée pour fournir une fin de dosage volumétrique précise.

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Contributions to the analytical chemistry of osmium and ruthenium—IX

The dimercapto derivatives of asymmetric triazine as colour reagents for osmium*

(*Received* 3 *November* 1969. *Accepted* 22 *December* 1969)

SPECTROPHOTOMETRIC determinations of osmium have been based upon its colour reactions with both inorganic and organic reagents. Whereas the number of inorganic reagents used for this purpose is relatively limited, the number of organic reagents is great. Among them the derivatives of thiourea,[1] thiosemicarbazide[2,3] and thiosemicarbazone[4-6] hold a prominent place.

Recently, by the substitution of selenium for the sulphur atom in the molecule of the organic reagent, new derivatives, which give coloured compounds with osmium, were obtained.[7,8] The sensitivity of these colour reactions does not differ too much from that of the reactions of the similar sulphur derivatives.

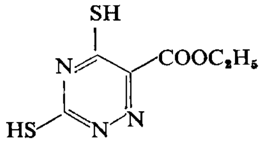
Concomitantly with aliphatic mercapto derivatives some heterocyclic mercapto derivatives such as 2-mercaptobenzimidazole[9] and asymmetric mercaptotriazines have begun to be used for the spectrophotometric determination of osmium.

In previous papers[3,10-12] the colour reactions of osmium with some mercapto derivatives of the asymmetric triazine class were reported. They may be classified in the three groups shown in Table I, from which it can be seen that for each group of reagents the substituents in the positions 3 and 5 of the triazine ring are the same, while the substituent in position 6 can be any radical.

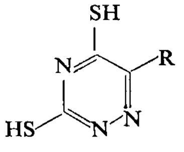
Table I summarizes the radicals attached in position 6 to the three main rings, and also shows 2-methyl-3,5-dihydroxy-6-mercapto-1,2,4-triazine in group *C*.

The location of this compound in reagent group *C* is justified by the fact that it is derived from one of the tautomeric forms of *C*.

The present paper reports the results of a study of the colour reaction of osmium with a new triazine derivative, namely 3,5-dimercapto-6-(ethylcarboxyl)-1,2,4-triazine (I),[13] which may be regarded as a member of a fourth group of 6-substituted triazine derivatives (II), the colour reactions of which with osmium are going to be studied.



I



II

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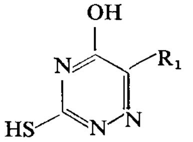
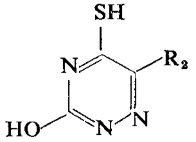
[*] Paper presented at the National Conference of Analytical Chemistry, Mamaia 1969 (Romania).

TABLE I.—REAGENTS FOR OSMIUM

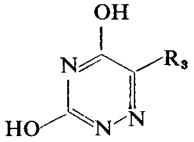
Group *A*

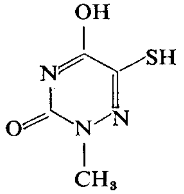


Group *B*



Group *C*



No.	R_1	R_2	R_3
1	H	H	H
2	CH_3	SCH_3	SCH_3
3	$(CH_3)_2$	SC_2H_5	SC_4H_9
4	COOH	SC_4H_9	$SCH_2CH{=}CH_2$
5	$COOC_2H_5$	$SCH_2C_6H_5$	SH
6	CH_2COOH	C_6H_5	
7	$CH_2COOC_2H_5$	$(CH_2)_5CH_3$	
8	$CH_2SCH_2C_6H_5$	$N(CH_2)_4O$	

EXPERIMENTAL

Reagents

Osmium solution, 2990 ppm. Prepared by dissolving osmium tetroxide in 0·2*M* sodium hydroxide, and standardized by Klobbie's method.[14] Test solutions of various concentrations were obtained by dilution with 0·2*M* sodium hydroxide.

Reagent solution, 0·1%. Prepared in 0·2*M* sodium hydroxide.

Metal ion solution. Aqueous solutions of commercially obtained $RuCl_3$, $PdCl_2$, H_2PtCl_6, $AuCl_3$, and $UO_2(NO_3)_2{\cdot}6H_2O$.

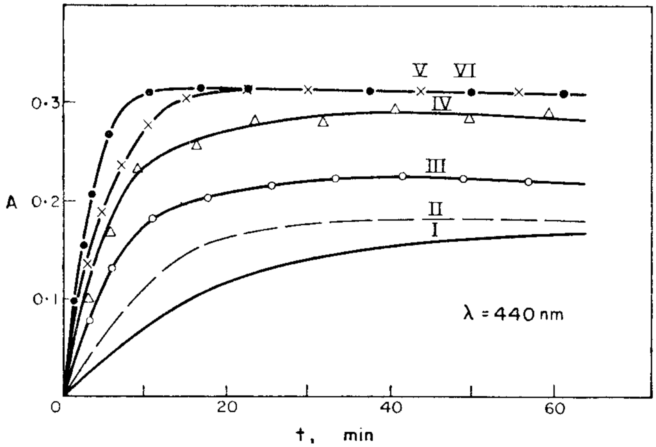


FIG. 1.—Effect of sulphuric acid concentration on rate of colour development. I—10^{-2}*M*; II—1*M*; III—2*M*; IV—3*M*; V—4*M*; VI—5*M*; 2 ml added per 25 ml total volume.

Procedures

To 25-ml graduated flasks osmium, reagent and sulphuric acid solutions were added in that order and the mixture was made up to the mark with distilled water.

For study of the effect of reagent concentration the mixtures contained 150 μg of osmium, 2 ml of 5*M* sulphuric acid and various amounts of 0·1% reagent solution. For study of the effect of acid concentration the solutions contained 150 μg of osmium, 3 ml of 0·1% reagent solution and 2 ml of sulphuric acid of various concentrations.

The absorption spectrum of the resulting coloured compound was measured against a blank solution on a sample containing 150 μg of osmium, 3 ml of 0·1% reagent solution and 2 ml of 5*M* sulphuric acid, made up to 25 ml with distilled water. The absorption spectrum of the blank (the reagent under the conditions of the reaction) was measured against water.

The effect of osmium concentration was studied by taking various amounts of osmium, 3 ml of 0·1% reagent solution and 2 ml of 5*M* sulphuric acid in 25 ml total volume.

RESULTS AND DISCUSSION

A volume of 3 ml of 0·1% reagent solution was found sufficient for complete reaction over the range of osmium concentration studied.

The results of some of the experiments to determine the effect of acidity are shown in Fig. 1, which shows that with rise in acid concentration in the sample, the rate of reaction and the intensity of colour both increase. The time needed for full colour development is reduced to less than 10 min when the concentration of the acid added is higher than 4*M*. The addition of acid more concentrated than 4*M* does not substantially change the maximum value of absorbance. It was therefore decided to add 2 ml of 5*M* sulphuric acid per 25 ml total volume.

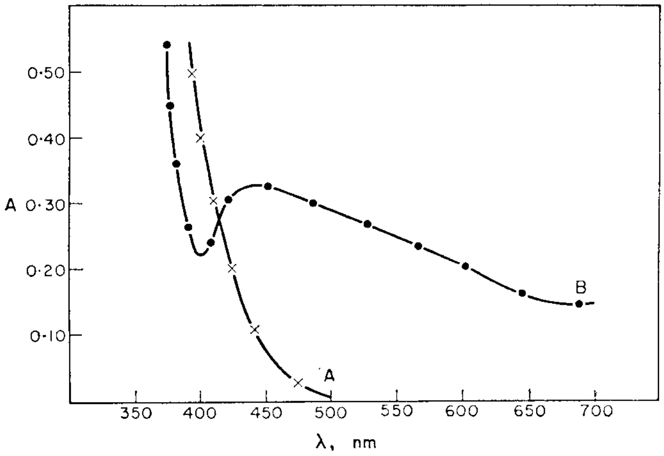


Fig. 2.—Absorption spectra.
A—Reagent *vs.* water.
B—Coloured compound *vs.* blank.

Absorption spectra

Figure 2 shows the absorption spectrum of the reagent *vs.* water under the conditions of the reaction (curve A), and of the resultant coloured compound against the blank (curve B).

This plot shows that the sensitivity is maximal between about 440 and 550 nm. We selected 440 nm as the wavelength for measurements.

On comparing the colour reaction of osmium with this derivative and the previously studied reaction with the similar compound of group *A*,[10] which contained the —OH group instead of the —SH group in position 5 of the triazine ring, it may be concluded that this change of group does not substantially change the position and the number of absorption bands.

Beer's law is obeyed over the range 0·5–18·0 ppm osmium at 440 nm and 0·7–18·0 ppm at 560 nm respectively, the corresponding absorbance for concentrations of 18·0 ppm being 0·97 and 0·73.

Comparison of the sensitivity of this reaction and that of the reaction using the similar reagent of the triazine group *A* shows that the substitution of the —SH group for the —OH group substantially increases the sensitivity, the lower concentration limit falling from 1·5 to 0·5 ppm.

Interferences

The study of the effect of the ions UO_2^{2+}, Pd^{2+}, Pt^{4+}, Ru^{3+}, Au^{3+} on the colour reaction of osmium with the reagent showed the following: the ions UO_2^{2+}, Ru^{3+} and Au^{3+} do not form a similarly coloured complex but inhibit the determination; Pd^{2+} interferes by forming a precipitate; Pt^{4+} can be tolerated up to Os:Pt ratios of 1:6.

The composition of the compound

The method of continuous variations[15] and the method of spectrophotometric titration[16] both suggested that the ratio Os:R is 1:2.

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Summary—The parameters of the reaction of osmium with 3,5-dimercapto-6-(ethylcarboxy)-1,2,4-triazine have been studied and the optimum conditions for the spectrophotometric determination of osmium over the range 0·5–18·0 ppm determined. The coloured product contains the components in the ratio 1:2 metal:ligand.

Zusammenfassung—Die Parameter der Reaktion von Osmium mit 3,5-Dimercapto-6-äthylcarboxy-1,2,4-triazin wurden untersucht und die optimalen Bedingungen zur spektrophotometrischen Bestimmung von Osmium im Bereich 0,5–18,0 ppm ermittelt. Die farbige Verbindung enthält die Komponenten im Verhältnis Metall:Ligand = 1 : 2.

Résumé—On a étudié les paramètres de la réaction de l'osmium avec la 3,5–dimercapto 6–(éthylcarboxy) 1,2,4–triazine et déterminé les conditions optimales pour le dosage spectrophotométrique de l'osmium dans le domaine 0,5–18,0 p.p.m. Le produit coloré renferme les composants dans le rapport 1:2, métal:ligand.

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Submicro determination of aluminium, bismuth and copper in organometallic compounds*

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THE RANGE of organometallic materials analysed on the submicro scale has now been extended to those containing aluminium, bismuth and copper.

For reasons discussed earlier,[1] photometric titration of the metals after digestion of organic materials was not pursued, suitable spectrophotometric procedures being available, but both open and closed tube digestion procedures were attempted.

EXPERIMENTAL

Spectrophotometric methods

Aluminium. From previous experience, it was considered that methods involving lake formation and stabilizing agents[2,3] would not be suitable, and the most promising alternative appeared to be extraction of the 8-hydroxyquinoline (oxine) complex.[3] A single extraction from a solution at pH 5·2 gave consistent results over the range 1·5–10·5 μg of metal provided that the shaking time during extraction was controlled. Particular attention had to be paid to cleanliness of apparatus to retain the required repeatability of results. Separatory funnels and cuvettes were washed successively with chloroform, distilled water, concentrated nitric acid, distilled water and acetone.

Bismuth. The thiourea and iodide methods of Lisicki and Boltz[4] were examined. Volumes of reagents and final solutions were halved and absorbances measured in 40-mm cells in order to approach the required sensitivity. The thiourea method was not successful; on the other hand, although sensitivity was not very high, the iodide method gave results of sufficient consistency to warrant its adoption. To prevent hydrolysis and to bring the acid concentration up to that recommended for the final solution, 10 ml of 5*N* sulphuric acid were used to rinse out the digestion tubes into the volumetric flasks.

Copper. Three extraction techniques were considered. Use of diethyldithiocarbamate[5] was not very successful; 2,2-diquinolyl[6] was too insensitive for present purposes but a modification of the technique described by Tuck and Osborn,[6] using neocuproine, was successfully developed. It was found, however, that use of bis-cyclohexanone oxalyldihydrazone,[7] which required no extraction, was not only simpler but more sensitive and repeatable when the buffer recommended by Somers and Garraway[8] was used.

Mineralization procedures

Open-tube digestion with perchloric/sulphuric acid mixture gave satisfactory results for the bismuth compounds but low and variable results for the copper and aluminium compounds, particularly the latter. Sealed-tube digestion with nitric/sulphuric acid mixture, however, gave satisfactory results for all the compounds.

Recommended procedures

Mineralization. Digest the samples, containing 4–20 μg of metal for bismuth or copper compounds or 1·5–10·5 μg of aluminium, in sealed tubes by the procedure described elsewhere.[9,10]

Determination of aluminium. Transfer the residue from the digestion tube into a 50-ml separatory funnel with about 10 ml of water. Add 5 ml of buffer solution (30 g of sodium acetate trihydrate in 420 ml of water plus 60 ml of 0·5*M* acetic acid). By pipette add 10 ml of a 0·25% chloroform solution of oxine to the funnel, stopper and shake it for 3 min. Allow the layers to separate and allow the organic layer to flow into a 30-mm stoppered spectrophotometer cuvette through a plug of cotton wool in the stem of the funnel. Measure the absorbance at 395 nm against a reference blank solution taken through the whole procedure. Prepare a calibration curve by applying the colour development procedure to a standard aluminium solution.

Determination of bismuth. Transfer the residue from the digestion tube into a 25-ml volumetric flask with 10 ml of 5*N* sulphuric acid. Add 10 ml of iodide–ascorbic acid reagent (140 g of potassium iodide and 10 g of ascorbic acid dissolved in water and diluted to 1 litre). Dilute to the mark and

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measure the absorbance at 337 nm in a 40-mm cuvette against a reference blank solution taken through the whole procedure. Prepare a calibration curve by applying the colour development procedure to portions of standardized[11] bismuth solution.

Determination of copper. Transfer the residue from the digestion tube into a 25-ml volumetric flask with about 10 ml of water. Add, in quick succession, 0·2 ml of 10% ammonium citrate solution, one drop of 0·02% aqueous Neutral Red solution, 3*M* sodium hydroxide dropwise until the indicator changes colour, 5 ml of buffer solution (400 ml of 0·5*M* boric acid and 60 ml of 0·5*M* sodium hydroxide) and, finally, 1 ml of 0·2% bis-cyclohexanone oxalyldihydrazone solution in 50% ethanol. After 20 min, dilute to the mark and measure the absorbance at 595 nm in a 40-mm cuvette against a reference blank solution taken through the whole procedure. Prepare a calibration curve by applying the colour development procedure to a standard copper solution.

RESULTS AND DISCUSSION

The results of the analysis of a number of organometallic compounds by the recommended methods are summarized in Table I. Two of the 44 determinations done fell just outside the normally accepted limits, of ±0·3% absolute, for microanalysis of organic compounds.

TABLE I.—ANALYSIS OF ORGANOMETALLIC COMPOUNDS

Compound	Range of weight, μg	Metal, %		Range of errors, % absolute
		Calc.	Found, mean*	
Al acetylacetonate	78·3–95·9	8·31	$8{\cdot}3_4$	$-0{\cdot}0_9$ to $+0{\cdot}1_6$
Al *N*-benzoyl-*N*-phenylhydroxylaminate	90·8–103·2	4·06	$3{\cdot}9_9$	$-0{\cdot}1_6$ to $+0{\cdot}0_1$
Al oxinate	72·0–107·3	5·87	$5{\cdot}9_3$	$-0{\cdot}0_3$ to $+0{\cdot}1_7$
Bi 7,8-benzoquinoline iodide	39·9–77·8	23·30	$23{\cdot}2_2$	$-0{\cdot}1_5$ to $-0{\cdot}0_2$
Bi mercaptobenzothiazole	38·9–55·3	29·53	$29{\cdot}5_8$	$-0{\cdot}3_1$ to $+0{\cdot}3_2$
Bi oxinate	50·4–70·7	31·69	$31{\cdot}6_9$	$-0{\cdot}0_8$ to $+0{\cdot}0_8$
Cu acetylacetonate	52·2–85·8	24·27	$24{\cdot}2_5$	$-0{\cdot}2_7$ to $+0{\cdot}2_9$
Cu *N*-benzoyl-*N*-phenylhydroxylaminate	59·7–77·9	13·02	$13{\cdot}0_0$	$-0{\cdot}1_8$ to $+0{\cdot}2_8$
Cu pyridinethiocyanate	82·4–100·6	18·80	$18{\cdot}7_8$	$-0{\cdot}2_6$ to $+0{\cdot}1_6$
Cu quinaldinate	70·6–77·5	14·92	$14{\cdot}8_9$	$-0{\cdot}2_8$ to $+0{\cdot}2_3$
Cu salicylaldoximate	72·6–86·6	18·92	$18{\cdot}8_5$	$-0{\cdot}1_8$ to $-0{\cdot}0_1$

* Of 4 results.

Although good results were obtained for the analysis of bismuth compounds after open-tube digestion with perchloric/sulphuric acid mixture, those for the copper compounds tended to be low (average recovery 98·6%) whilst those for aluminium compounds were very low and erratic. Open-tube digestion is, however, manipulatively simpler and more rapid than the sealed-tube technique; attempts are being made to modify the procedure so far employed, so as to produce a generally applicable method.

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Summary—Methods for the determination of aluminium, bismuth or copper in samples of organometallic compounds weighing 40–110 μg have been developed. Spectrophotometric determination following digestion with nitric and sulphuric acids in a sealed tube is recommended, all results obtained from the analysis of standard compounds being within ±0·3% absolute error. Digestion in an open tube with perchloric and sulphuric acids gives satisfactory results for bismuth compounds but erratic and often low results for aluminium and copper compounds.

Zusammenfassung—Zur Bestimmung von Aluminium, Wismut oder Kupfer in Proben metallorganischer Verbindungen, die 40–110 μg wiegen, wurden Verfahren entwickelt. Es wird empfohlen, an einen Aufschluß mit Salpeter- und Schwefelsäure im verschlossenen Rohr eine spektrophotometrische Bestimmung anzuschließen; alle Ergebnisse der Analyse von Standardverbindungen lagen innerhalb ±0,3 prozent absolutem Fehler. Aufschluß mit Perchlorsäure im offenen Rohr gibt bei Wismutverbindungen zufriedenstellende, bei Aluminium- und Kupferverbindungen jedoch stark streuende und oft zu niedrige Ergebnisse.

Résumé—On a élaboré des méthodes pour la détermination d'aluminium, bismuth ou cuivre dans des échantillons de composés organométalliques pesant 40–110 μg. On recommande la détermination spectrophotométrique suivant la digestion avec les acides nitrique et sulfurique en tube scellé, tous les résultats obtenus de l'analyse de composés étalons étant d'erreur absolue comprise dans les limites ±0,3%. La digestion dans un tube ouvert avec les acides perchlorique et sulfurique donne des résultats satisfaisants pour les composés du bismuth mais des résultats variables et souvent faibles pour les composés de l'aluminium et du cuivre.

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Fällung des Wismuts als Bis(triphenylselenonium)-Pentachlorobismutat (III)

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Innerhalb verschiedener wasserlöslicher Komplexe (Gutbier und Müller[1]): $[BiCl_4]^-$, $[BiCl_5]^{2-}$, $[BiCl_6]^{3-}$ und verschiedener mehrkerniger Ionen schreiben Remy und Pellens[2] dem Pentachlorobismutat die größte Stabilität zu. Mit aliphatisch substituierten Ammoniumsalzen wird das Wismut aus salzsauren Lösungen als Tetrachlorokomplex gefällt und kann zu extraktiv-photometrischen

Bestimmungen[3] in dieser Form separiert werden ($[HN(C_4H_9)_3]\,[BiCl_4]$, $\lambda_{max}/CH_2Cl_2 = 330$ nm), Triphenylselenoniumionen scheiden jedoch das, eutspechend, extrahierbare Pentachloroanion ab. $[(C_6H_5)_3Se]_2$: $[BiCl_5]$, $\lambda_{max}/CH_2Cl_2 = 340$ nm.

Unter den Triphenylselenoniumsalzen anderer komplexer Halogenometallsäuren (Tabelle I) weist die Mehrzahl in wäßrigen Medien deutlich hervortretende Löslichkeiten auf. Aus 10%-ig Kalium- bzw. Natriumchlorid-haltigen Lösungen beginnt die Fällbarkeit des Kupfers, Kobalts, Zinks und Cadmiums erst bei Metallgehalten ab 2%. Leichter fällbar sind die entsprechenden Salze von Halogenosäuren dreiwertiger Metalle. In Citrat-haltigen, schwach sauren Medien sind jedoch alle leicht komplex löslich außer $[(C_6H_5)_3Se]_2\,[BiCl_5]$ und $[(C_6H_5)_3Se]_2\,[BiBr_5]$. Im ammoniakalischen Bereich werden auch diese durch Citrat leicht gelöst.

TABELLE I.

Metall	Verbindung	Farbe	Schmelzpunkt, °C
Kupfer	$[(C_6H_5)_3Se]_2[CuCl_4]$	gelb	214–216 (Zers.)
	$[(C_6H_5)_3Se]_2[CuBr_4]$	schwarz-violett	197–199
Kobalt	$[(C_6H_5)_3Se]_2[CoCl_4]$	blau	276–278
	$[(C_6H_5)_3Se]_2[CoBr_4]$	grün	259–260
Zink	$[(C_6H_5)_3Se]_2[ZnCl_4]$	farblos	287–289
	$[(C_6H_5)_3Se]_2[ZnBr_4]$	farblos	261–263
Cadmium	$[(C_6H_5)_3Se]_2[CdCl_4]$	farblos	278–279
	$[(C_6H_5)_3Se]_2[CdBr_4]$	farblos	248–249
Blei	$[(C_6H_5)_3Se]_2[PbCl_4]$	farblos	215–216
Mangan(III)	$[(C_6H_5)_3Se]_2[MnCl_5]$	grün	—
Eisen(III)	$[(C_6H_5)_3Se][FeCl_4]$	gelb	—
	$[(C_6H_5)_3Se][FeBr_4]$	dunkelbraun	134–135
Antimon(III)	$[(C_6H_5)_3Se]_2[SbCl_5]$	farblos	—
Wismut	$[(C_6H_5)_3Se]_2[BiCl_5]$	farblos	278–280
	$[(C_6H_5)_3Se]_2[BiBr_5]$	blaßgelb	259–260

Eine von Burkhalter und Solarek[4] ausgearbeitete Bestimmungsmethode für Wismut als Trimethylphenylammonium-Tetrajodobismutat(III) $[(CH_3)_3(C_6H_5)N]\,[BiJ_4]\,H_2O$ bietet keine Trennungsmöglichkeiten von Übergangsmetallionen, außerdem stört die Anwesenheit anderer Halogenionen.

EXPERIMENTELLER TEIL

Reagentien

Triphenylselenoniumchlorid, 20%ig *wässrige Lösung.* Sie wird unter gelegentlichem Umrühren 2–3 Stunden mit Aktivkohle auf dem Wasserbad erwärmt. Die filtrierte, wasserhelle Lösung ist mindestens 3 Monate haltbar. Zur Fällung des Wismuts verdünnt man sie mit 1*M* Salzsäure im Verhaltnis 1:1.

Zitronensäure bzw. *Trinatriumcitrat.*

Ammoniumchlorid, 15%ig *wässrige Lösung.*

Waschlösung. Triphenylselenoniumchlorid (2g) und Zitronensäure (0,5 g) in 100 ml 0,2*M* Salzsäure.

Salzsäure, 0,2*M.*

Wismut-Standardlösung. Die erforderliche Menge Wismut *p.a.* (z.B. Baker 99,95% bezw. 99,999% Bi) wird mit konz. Salpetersäure gelöst. Man dampft bis zur beginnenden Trockne ein, und nimmt mit dem gewünschten Volumen 0,7*M* Salpetersäure auf.

Aus Wismutnitrat mit verd. Salpetersäure bereitete lösungen werden komplexometrisch eingestellt, unter Gebrauch von Brenzkatechinviolett als Indikator. Dieses Verfahren setzt die Abwesenheit von Chloridionen voraus.

Arbeitsvorschrift

Die salpeter-, oder salzsaure Probelösung, die 15–60 mg Wismut(III) enthalten mag, und deren Acidität zwischen 0,2 und 1*N* liegt, wird im Becherglas von 400–600 ml Inhalt bei Aciditäten $<0{,}5N$ mit 4 g Citronensäure und beim Vorliegen solcher $\geqslant 0{,}5N$, mit 5 g Trinatriumcitrat versetzt. Nach deren Auflösung verdünnt man mit Wasser unter Rühren auf etwa 150 ml und fügt ebenfalls unter Rühren 20 ml Ammoniumchlorid-Lösung hinzu.

Die Fällung des Wismuts erfolgt bei Raumtemperatur durch langsames Zutropfen von 15 ml 0,5*M* salzsaurer Lösung des Triphenylselenoniumchlorids unter Umrühren. Der anfänglich flockig-voluminöse Niederschlag wird gegen Ende der Reagenzzugabe feinkristallin. Man rührt mehrmal, um, und beläßt eine Stunde bei Raumtemperatur. Nach dieser Zeit ist die überstehende Lösung klars der Niederschlag hat sich gut abgesetzt.

Man filtriert nun den aufgewirbelten Niederschlag durch einen bei 110° zur Gewichtskonstanz getrockneten Filtertiegel der Frittendichte G4, und benutzt zum vollständigen Überführen und Waschen 50 ml Waschlösung. Durch nur mässig starkes Trockensaugenwird Rissbildung in der Niederschlags-schichte vermieden. Man wäscht zweimal mit je 5 ml 0,2*M* Salzsäure und saugt dann scharf ab.

Der Niederschlag wird im (belüfteten) Trockenschrank bei 110° in 60 min bis zur Gewichtskonstanz getrocknet. Umrechnungsfaktor für Wismut beträgt 0,2077. Zur Säuberung der Fritten eignet sich raschlösende ammoniakalische Citratlösung, nicht Chromschwefelsäure.

Der mittlere Fehler für die Bestimmung des Metalls aus reinen Lösungen liegt bei 0,3 %.

Spezifität und Vorteile der Methode

Unter genannten Arbeitsbedingungen wird Wismut bereits aus 5×10^{-3}%-igen Lösungen quantitativ abgeschieden. Dabei sind Schwankungen der Salzsaurekonzentration zwischen 0,1 und 1*M* tragbar. Citrat hält in noch schwächer sauren oder alkalischen Lösungen (nach Aufschlüssen mit

TABELLE II.

Wismut, *mg*		Fehler			Verhältnis
gegeben	gefunden	%	Fremdion, *mg*		Fremdion:Bi^{3+}
29,0	$29{,}3_5$	+1,2	Chlorid	10000	350
29,0	28,8	−0,7	Nitrat	2900	100
30,0	29,6	−1,3	Sulfat	1500	50
30,0	29,8	−0,7	Phosphat	1500	50
20,0	20,2	+0,8	Citrat	2000	100
20,0	20,1	+0,7	Citrat	4000	200
48,4	$48{,}2_5$	−0,3	Tartrat	4000	80
40,0	$40{,}2_5$	+0,6	Co^{2+}	40	1
29,0	$28{,}8_5$	−0,5		145	5
20,0	$19{,}8_5$	−0,8		200	10
29,0	29,3	+1	Ni^{2+}	145	5
20,0	$19{,}8_5$	−0,8		200	10
40,0	40,3	+0,8	Mn^{2+}	40	1
29,0	28,8	−0,8		290	10
38,7	39,0	+0,8	Al^{3+}	200	5
30,0	29,8	−0,7		300	10
$19{,}3_5$	19,5	+0,8		400	20
50,0	49,7	−0,6	Fe^{3+}	50	1
20,0	$19{,}8_5$	−0,9		100	5
20,0	$20{,}1_5$	+0,8		200	10
20,0	$20{,}1_5$	+0,8	Cr^{3+}	100	5
30,0	$29{,}8_5$	−0,5		3000	10
39,0	$38{,}9_5$	−0,2	Cu^{2+}	39	1
30,0	$30{,}2_5$	+0,8		150	5
20,0	20,2	+1		200	10
20,0	20,2	+1	Pb^{2+}	20	1
40,0	40,8	+2		80	2
50,0	49,7	−0,6	As(III)	50	1
29,0	$28{,}9_5$	−0,2		145	5
20,0	$20{,}0_5$	+0,4	Sb^{3+}	20	1
39,0	39,6	+1,6		80	2
30,0	$30{,}1_5$	+0,6	Te(IV)	60	2
40,0	39,8	−0,5	Th^{4+}	40	1
$19{,}3_5$	$19{,}5_5$	+1,1		100	5
39,0	39,1	+0,3	Mo(VI)	40	1

Natriumhydroxid) Wismut in Lösung, ohne Störungen zu verursachen. Da die Anionen der Mineralsäuren nicht stören (Tabelle II), können diese nach schließlichem Zusatz von Citrat mit Natriumhydroxidlösung bis in den pH-Bereich 0,5–1 abgestumpft werden. Bemerkenswert gering ist hierbei der Störeinfluß von Phosphat, sowie Eisen(III) und Chrom(III). Zink, Cadmium und Quecksilber(II) verursachen bei Verhältnissen Bi^{3+}:Fremdion = 1:1 Überbefunde, und man trennt dann das Wismut durch Vorfällung mit Ammoniak von den Ionen Zn^{2+} und Cd^{2+} ab. Größere Mengen Ble über das Verhältnis Bi:Pb = 1:1 hinausgehend trennt man am günstigsten durch den Aufschluß mit konz. Schwefelsäure ab. Das Verfahren eignet sich zur Analyse von Materialien mit Wismut-Gehalten ab etwa 5% Bi (Tabelle III).

TABELLE III.—WISMUTBESTIMMUNG IN TECHNISCHEN PRODUKTEN

Katalysator (Knappsack)		Weichlot	
SiO_2	51,8%	Pb	49,5%
MoO_3	17,0%	Sn	40,1%
Fe_2O_3	7,0%	Sb	0,42%
P_2O_5	1,04%	Cu	0,03%
Bi_2O_3	19,0%	Bi	9,8%
Bi_2O_3 gefunden	$19{,}0_5$%	Wismut gefunden	9,9%

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Zusammenfassung—Die Fällung des Wismuts als $[(C_6H_5)_3Se]_2[BiCl_5]$ ermöglicht bei Gegenwart von Citrat die gravimetrische Bestimmung von 15–50 mg Wismut und deren Trennung von mittleren Mengen zwei- und dreiwertiger Übergangsmetalle, sowie von Phosphat. Es wird der Aufbau verschiedener Triphenylselenonium Halogenokomplexe solcher Metalle ausgewiesen.

Summary—By precipitation as $[(C_6H_5)_3Se]_2[BiCl_5]$ in the presence of citrate, 15–50 mg of bismuth can be determined gravimetrically, and separated from moderate amounts of bi- and tervalent metals and from phosphate. Such metals are characterized by the formation of the triphenylselenonium salts of their various halide complexes.

Résumé—Par précipitation à l'état de $[(C_6H_5)_3Se]_2[BiCl_5]$ en la présence de citrate, on peut doser gravimétriquement 15–50 mg de bismuth et le séparer de quantités peu élevées de métaux di- et trivalents et de phosphate. Tels métaux sout characterisés par la formation des sels de triphénylsélénium de leurs divers complexes halogénés.

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Two new spectrophotometric reagents for copper

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IT HAS been known for many years that chromogens containing the methine or ferroin group may be transformed into reagents specific for copper(I) by alkyl, aryl, or amino substitution on the carbon atoms immediately contiguous to the chelating nitrogen atoms.[1-3] This effect has been attributed to steric hindrance which prevents octahedral co-ordination around iron(II) but allows tetrahedral co-ordination around copper(I).[1,2] Two more compounds have been prepared which exhibit this property: 6-methyl-2-pyridylhydrazidine and the hitherto unknown 3-(6-methyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine, hereafter referred to as MPH and MPTZ respectively. MPH reacts with copper(I) to give a fairly stable yellow compound ($\varepsilon = 700$ l.mole^{-1}.mm^{-1}; λ_{max} 426 nm) and MPTZ reacts to form a stable red-orange compound ($\varepsilon = 955$ l.mole^{-1}.mm^{-1}; λ_{max} 492 nm).

EXPERIMENTAL

Reagents

Preparation of MPH. MPH has been previously reported by van der Burg,[4] but in the present work, the method of Case[5] was used with the following modifications: 97% hydrazine and anhydrous isopropanol were employed in place of 95% hydrazine and 95% ethanol, and anhydrous magnesium sulphate was added to the reaction mixture. The crude product was recrystallized three times from boiling isopropanol. White plates were obtained, in 82% yield, m.p. 115°, in agreement with that reported by van der Burg. Calculated for $C_7H_{10}N_4$: C, 55·98%; H, 6·71%; N, 37·31%; found: C, 55·8%; H, 6·7%; N, 37·0%.

TABLE I.—DETERMINATION OF COPPER IN IRON-CONTAINING BOILER WATER

	Copper in sample, *ppm*	Copper added, *ppm*	Iron added, *ppm*	Copper found, *ppm*
By extraction of Cu(MPTZ)$_2^+$ into isopentanol	?	0	0	0·34
	0·34	0·50	0	0·85
	0·34	1·00	0	1·34
	0·34	1·50	0	1·86
	0·34	0	1·00	0·34
	0·34	0	10·0	0·35
	0·34	0	100·0	0·34
By Cu(MPH)$_2^+$ in aqueous solution	?	0	0	0·17
	0·17	0·50	0	0·68
	0·17	1·00	0	1·15
	0·17	1·50	0	1·69
	0·17	0	1·00	0·18
	0·17	0	10·0	0·17
	0·17	0	100·0	0·18
By extraction of Cu(MPH)$_2^+$ into isopentanol	?	0	0	0·17
	0·17	0·50	0	0·67
	0·17	1·00	0	1·15
	0·17	1·50	0	1·65
	0·17	0	1·00	0·16
	0·17	0	10·0	0·18
	0·17	0	100·0	0·17

All analyses were performed in triplicate on the same sample of boiler effluent. The sample was diluted 1:1 with standard copper and iron solutions or demineralized water for the determinations with MPH.

Preparation of MPTZ. The method of Case[5] was used with the following modifications: isopropanol was used as the solvent for the MPH and a mixture of 1:5 methanol–isopropanol was used as the solvent for the benzil. The crude yellow product was recrystallized three times from boiling benzene. Slightly yellow crystals were obtained, in 68% yield, m.p. 179°. Calculated for $C_{21}H_{16}N_4 \cdot H_2O$: C, 73·69%; H, 5·27%; N, 16·31%; found: C, 73·6%; H, 5·4%; N, 16·1%.

MPH reagent solution, 0·02*M*. Dissolve 0·30 g of MPH in 50 ml of isopropanol and dilute to 100 ml with copper-free water.

MPTZ reagent solution, 0·02*M*. Dissolve 0·65 g of MPTZ in 90 ml of boiling methanol. Cool to room temperature and dilute to 100 ml with methanol.

Phosphate buffer solution, pH 6·5, copper-free. Dissolve 10 g each of potassium dihydrogen phosphate and dipotassium hydrogen phosphate in water and dilute to 100 ml. Purify as below.

Phosphate buffer solution, pH 10, copper-free. Dissolve 10 g of dipotassium hydrogen phosphate in 50 ml of water, add 12·5 ml of 0·10*M* sodium hydroxide, dilute to 100 ml, and purify as below.

Hydroxylammonium chloride solution 10%, *copper-free.* Purified as below.

Sodium hydroxide solution, 5*M*.

Copper-free water. To 1 litre of distilled water, add 1 ml of MPTZ reagent solution, 1 ml of 10% hydroxylammonium chloride solution and 10 ml of pH 6·5 buffer solution. Extract with 50 ml of isopentanol. Discard the alcoholic phase.

Buffer and other aqueous solutions were purified by a similar procedure.

Standard copper solutions, 1000 *ppm.* Prepared from electrolytic grade copper, and freed from nitrate by fuming with sulphuric acid.

Procedures

Preparation of sample. Both MPH and $Cu(MPH)_2^+$ are soluble in water. $Cu(MPTZ)_2^+$ is somewhat soluble in water, but MPTZ itself is not water-soluble over the pH range of colour development. The nitrates and perchlorates of both complexes are insoluble in water, and those of $Cu(MPH)_2^+$ are extractable, whereas the extraction of $Cu(MPTZ)_2^+$ is independent of presence of perchlorate. Thus, when copper is to be determined in aqueous solution with MPH the dissolution procedure must avoid perchloric acid and nitrate ions must be removed if nitric acid is used. When the solvent extraction procedures are used, it is best to dissolve samples in nitric acid/perchloric acid mixture.

Colour development. Take a 100-ml aliquot of slightly acidic sample solution containing about 0·2 mg of copper. Add 1 ml of 10% hydroxylammonium chloride solution, and complete the determination by one of the following.

1. Add 1 ml of MPH reagent solution, 5 ml of pH 10 buffer solution, and dilute to a specific volume. Mix well and read the absorbance at 426 nm.
2. Add 1 ml of MPH reagent solution, 1 ml of pH 10 buffer solution, transfer quantitatively to a separatory funnel and extract with two 10-ml portions of isopentanol. Combine the extracts in a 25-ml volumetric flask and dilute to the mark with methanol. Mix well and read the absorbance at 426 nm.
3. Add 1 ml of MPTZ reagent solution, 1 ml of pH 6·5 buffer solution, transfer quantitatively to a separatory funnel and extract with 20 ml of isopentanol. Dilute the extract to 25 ml in a volumetric flask. Mix well and read the absorbance at 492 nm.

Calibration curves are constructed from standard solutions treated in the same manner.

RESULTS AND DISCUSSION

Synthesis. The method of Case[5] was modified because it was found that water in the reaction mixture for the preparation of MPH seemed to favour the formation of a secondary product (which was not characterized). For this reason, anhydrous hydrazine was used, anhydrous isopropanol was employed as the solvent and anhydrous magnesium sulphate was added to the reaction mixture. MPH and MPTZ are easier to synthesize than some of the more sensitive reagents which have been proposed.[4]

Colour. The colour of $Cu(MPH)_2^+$ is stable in isopentanol for about 6 hr, after which it begins to fade. The colour of $Cu(MPH)_2^+$ in water is stable for at least 12 hr, after which it begins to fade. The colour of $Cu(MPTZ)_2^+$ in isopentanol is stable for at least 24 hr. The spectral bands are broad. Beer's law is obeyed up to at least 12 ppm with MPH and 10 ppm with MPTZ.

Stoichiometry. Spectrophotometric titration shows that the species $Cu(MPH)_2^+$ and $Cu(MPTZ)_2^+$ are the colour-producing agents in solution. No coloured tris-complex of copper(I) with either reagent was detected at any pH studied.[1] It is possible that the copper is bonded through two nitrogen atoms per ligand to give a complex in which two five-membered rings at right angles to each other are formed.[1,2]

Effects of pH on complex formation. The yellow $Cu(MPH)_2^+$ species is completely formed in aqueous solution and in isopentanol between pH 8 and 11·5. The red-orange $Cu(MPTZ)_2^+$ species is completely formed in isopentanol when extracted from the aqueous phase at pH values between 4 and 10. The formation of both is markedly pH dependent outside these limits.

Suitability as spectrophotometric reagents for copper(I). These reagents are specific, reasonably sensitive and easy to prepare. Of cobalt, iron, nickel, cadmium, molybdenum, calcium, magnesium, chromium, manganese, aluminium, barium, strontium and platinum, only aluminium interferes by forming a precipitate with MPH and only aluminium and chromium interfere by forming a precipitate with MPTZ in a buffered solution. Since $Cu(MPH)_2^+$ and $Cu(MPTZ)_2^+$ can both be extracted, preferably into isopentanol, these interferences can be eliminated. Extraction also reduces the blank value. Ammonium ion, tris(hydroxymethyl)aminomethane, and 2-amino-2-methyl-1-propanol prevent or inhibit the colour development due to $Cu(MPH)_2^+$, probably by formation of non-dissociated complex species with copper(I).

One of the curious properties of MPH and MPTZ is that in contrast to many similar copper reagents, no coloured species are formed with cobalt(II).[1,4,6] Copper may be determined in the presence of 100 times as much iron, even without extraction. No other interferences have been found which cannot be eliminated by extraction. Of the ferroin-type reagents for copper in use at the present time, these two may be said to be among the simplest and least expensive to prepare and use, while giving reasonable sensitivity and maximum selectivity for copper.

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Summary—Two ferroin-type compounds are proposed as spectrophotometric reagents for copper(I): 6-methyl-2-pyridylhydrazidine, which forms a yellow complex with λ_{max} 426 nm and molar absorptivity 700 l.mole^{-1}.mm^{-1}, and 3-(6-methyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine, which forms a red-orange complex with λ_{max} 492 nm and molar absorptivity of 955 l.mole^{-1}.mm^{-1}. These reagents are specific for copper and the complexes can be extracted into isopentanol for increased sensitivity.

Résumé—On propose deux composés de type ferroïne comme réactifs spectrophotométriques pour le cuivre(I): la 6-méthyl 2-pyridylhydrazidine, qui forme un complexe jaune avec λ_{max} 426 nm et un coefficient d'absorption moléculaire de 700 l.mole^{-1}.mm^{-1}, et la 3-(6-méthyl-2-pyridyl)-5,6-diphényl-1,2,4-triazine, qui forme un complexe rouge-orangé avec λ_{max} 492 mm et un coefficient d'absorption moléculaire de 955 l.mole^{-1}.mm^{-1}. Ces réactifs sont spécifiques du cuivre et les complexes peuvent être extraits en isopentanol pour une sensibilité accrue.

Zusammenfassung—Zwei Verbindungen vom Ferrointyp werden als spektrophotometrische Reagentien für Kupfer(I) vorgeschlagen: 6-Methyl-2-pyridylhydrazdin, das einen gelben Komplex mit λ_{max} 426 nm und molarem Extinktionskoeffizienten 700 l. mol^{-1} mm^{-1}, sowie 3-(6-Methyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazin das, einen orangeroten Komplex mit λ_{max} 492 nm und molarem Extinktionskoeffizienten 955 l. mol^{-1}mm^{-1} bildet. Diese Reagentien sind für Kupfer spezifisch; zur Erhöhung der Empfindlichkeit können die Komplexe in Isopentanol extrahiert werden.

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Amperometric titration of Cd(II), Hg(II) and Zn(II) in molten alkali thiocyanates with electrolytically generated sulphide ions

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FUSED alkali thiocyanates as a solvent have been the subject of a number of investigations in recent years,[1–13] but a paucity of data exists in the literature concerning the precipitation reactions in this solvent.[10] In this work we have investigated the precipitation reactions of some cations [Cd(II), Hg(II), Sn(II), Tl(I) and Zn(II)] by sulphide ions in order to test the feasibility of their titration.

In order to avoid the disadvantages connected with the weighing of titrants, the sulphide ions were produced *in situ* by reduction of thiocyanate at a platinum electrode according to the reaction

$$SCN^- + 2e^- \rightarrow CN^- + S^{2-} \qquad (1)$$

the quantitative yield of which has been already checked.[8,9]

The apparatus used was similar to that described elsewhere.[14] In this work a further vessel (anodic compartment) is joined to the main cell (cathodic compartment) by means of a sintered-glass disk.

The quantity of solvent used in the cathodic vessel was about 50 g. The solvent mixture was the sodium thiocyanate–potassium thiocyanate eutectic prepared as described in a previous paper.[13] The solvent in the cell was maintained under vacuum for about 1 hr at a temperature of 443·0 ± 0·2K. The solutes were introduced as pure salts or as pellets of sodium thiocyanate–potassium thiocyanate mixture containing a known weight of metal salts. The concentration of the solutions studied was always in the molality range 3×10^{-4}–2×10^{-3}.

In order to perform electrolysis, platinum electrodes 200 mm^2 in area were used. The current for the production of sulphide ions was supplied by a constant-current electronic generator and measured potentiometrically through the resistance drop across an AEG 100-ohm precision resistor connected in series. The maximum current density was 15 μA/mm^2. Greater current density was not used, in order to prevent sodium ion reduction.[8]

The titration curves were determined amperometrically by recording the diffusion current of the cations by means of a three-electrode Amel model 557/SU polarograph and a Graphispot type GRVAM galvanometric recorder. The potentials were measured *vs.* the glass reference electrode[15,16] standardized as described earlier.[13]

Quantitative results have been obtained for cadmium, mercury and zinc ions, which gave well defined titration curves; typical plots for cadmium and zinc are presented in Fig. 1.

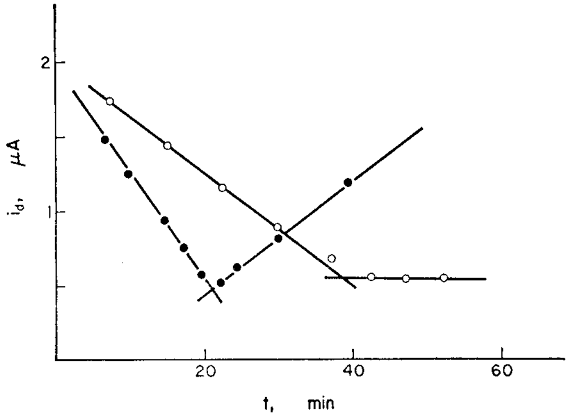

FIG. 1.—Amperometric titration curves of Zn(II) (full points) at −1·0 V and Cd(II) (open circles) at −0·6 V *vs.* Ag/Ag(I) (1*m*).

After the equivalence point the plots of these curves have different slopes, depending on the diffusion potentials of the cations examined. These potentials can lie in the anodic or cathodic branch or in the null current range of the irreversible composite wave which is probably due to the sulphide–polysulphide system. The polysulphide ions, which according to Metzger[9] are probably present, may be formed after the equivalence point from the sulphide ions and sulphur produced by thermal decomposition of the solvent.

The results obtained are summarized in Table I.

TABLE I

Cation	Number of titrations	Concentration range (molality)	S^{2-}Me(II) mean ratio
Cd(II)	5	5×10^{-4}–2×10^{-3}	1·007
Zn(II)	4	3×10^{-4}–2×10^{-3}	0·982
Hg(II)	3	5×10^{-4}–2×10^{-3}	0·986

In all the titrations the error was always smaller than ±2·5%. Obviously, this result demonstrates that the cyanide ion produced by reaction (1) does not interfere in the precipitation reactions.

On the contrary very large (negative) titration errors have been always obtained for tin(II) and thallium(I) ions.

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Summary—The feasibility of the titration of some cations in molten sodium thiocyanate–potassium thiocyanate mixture with electrolytically generated sulphide ions has been tested at 443 K. Quantitative data are given for the titration of cadmium, mercury and zinc ions.

Zusammenfassung—Die Möglichkeit der Titration einiger Kationen in einer Schmelze aus Natrium- und Kaliumthiocyanat mit elektrolytisch erzeugten Sulfidionen wurde bei 443°K geprüft. Quantitative Daten werden für die Titration von Cadmium-Quecksilber- und Zinkionen angegeben.

Résumé—On a essayé la possibilité du titrage à 443°K de quelques cations dans un mélange fondu de thiocyanate de sodium–thiocyanate de potassium avec des ions sulfure engendrés électrolytiquement. On fournit des données quantitatives pour le titrage des ions cadmium, mercure et zinc.

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New chromogens of the ferroin type—VI

Some derivatives of 1- and 3-cyanoisoquinoline and substituted 2-cyanopyridines

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A variety of new compounds containing the ferroin reacting group (—N=C—C=N—) has recently been synthesized by Case, including some triazines and benzimidazoles from 1- and 3-cyanoisoquinolines,[1] certain new diphenyl and bis(2-pyridyl)-1,2,4-triazines,[2] and some substituted pyridyl tetrazines and pyridazines.[3] As part of a continuing study and search for superior colorimetric reagents, the chromogenic reactions of these new compounds with iron(II), copper(I), and cobalt(II) have been examined spectrophotometrically. The results are reported in this brief communication.

Structures of the compounds studied (omitted here for brevity) can be found in the original papers by Case.[1,2,3] For simplicity the compounds (listed below) will be referred to by numeral.

I 6-Methylpicolinimidic acid hydrazide
II 6-Phenylpicolinimidic acid hydrazide
III 3-Isoquinolinecarboximidic acid hydrazide
IV 3-(6-Methyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine
V 3-(6-Phenyl-2-pyridyl)5,6-diphenyl-1,2,4-triazine
VI 3-(3-Isoquinolyl)-5,6-diphenyl-1,2,4-triazine
VII 3-(6-Methyl-2-pyridyl)-5,6-bis(2-pyridyl)-1,2,4-triazine
VIII 3-(6-Phenyl-2-pyridyl)-5,6-bis(2-pyridyl)-1,2,4-triazine
IX 3-(3-Isoquinolyl)-5,6-bis(2-pyridyl)-1,2,4-triazine
X 3-(3-Isoquinolyl)-1,2,4-triazino[5,6-*f*][4,7]phenanthroline
XI 3-(2-Pyridyl)-5-phenyl-6-(2-pyridyl)-1,2,4-triazine
XII 3-(4-Methyl-2-pyridyl)-5-phenyl-6-(2-pyridyl)-1,2,4-triazine
XIII 3-(4-Phenyl-2-pyridyl)-5-phenyl-6-(2-pyridyl)-1,2,4-triazine
XIV 2-(1-Isoquinolyl) benzimidazole
XV 2-(3-Isoquinolyl) benzimidazole
XVI 2-(1-Isoquinolyl)-3*H*-imidazo[4,5-*h*] quinoline
XVII 2-(3-Isoquinolyl)-3*H*-imidazo[4,5-*h*] quinoline
XVIII 2-(1-Isoquinolyl)-1*H*-imidazo[4,5-*c*] pyridine
XIX 2-(3-Isoquinolyl)-1*H*-imidazo[4,5-*c*] pyridine
XX 2-(1-Isoquinolyl)-5(6)-phenylbenzimidazole
XXI 2-(3-Isoquinolyl)-5(6)-phenylbenzimidazole
XXII 2,4-Diamino-6-(1-isoquinolyl)-1,3,5-triazine
XXIII 2,4-Diamino-6-(3-isoquinolyl)-1,3,5-triazine
XXIV 2-Amino-4,6-bis(1-isoquinolyl)-1,3,5-triazine
XXV 3,6-Bis(4-methyl-2-pyridyl)-dihydro-1,2,4,5-tetrazine
XXVI 3,6-Bis(4-ethyl-2-pyridyl)-dihydro-1,2,4,5-tetrazine
XXVII 3,6-Bis(4-phenyl-2-pyridyl)-dihydro-1,2,4,5-tetrazine
XXVIII 3,6-Bis(4-methyl-2-pyridyl)-1,2,4,5-tetrazine
XXIX 3,6-Bis(4-ethyl-2-pyridyl)-1,2,4,5-tetrazine
XXX 3,6-Bis(4-phenyl-2-pyridyl)-1,2,4,5-tetrazine
XXXI 3,6-Bis(4-methyl-2-pyridyl)-4-phenylpyridazine
XXXII 3,6-Bis(4-phenyl-2-pyridyl)-4-phenylpyridazine

EXPERIMENTAL

Preparative details and elemental analyses of the compounds studied were reported by Case.[1,2,3] The various standard solutions, pH buffers, reagents, and procedures used in this investigation are described in an earlier communication of this series.[4] Mole ratio and conditional formation constants (in ethanol–water mixtures) were determined spectrophotometrically by the method of continuous variations.

RESULTS AND DISCUSSION

All the compounds readily form coloured complexes except the difficultly soluble **XXVII** and **XXX**. As expected on the basis of their structures and the steric requirements for chelation, compounds **I**, **II**, **IV** and **V** do not form coloured complexes with either cobalt(II) or iron(II) but do with copper(I). The pH ranges for colour formation are generally broad. The iron(II) chelates form rapidly between pH 2 and 9, with maximum colour production at pH 5–8. The only exceptions are the iron(II) chelates of **X**, **XXV** and **XXVI** which exhibit maximum colour between pH 3 and 5. Formation of the copper(I) and cobalt(II) chelates occurs rapidly between pH 3 and 11. Maximum colour production results at pH 5–8 for copper and 5–11 for cobalt.

Most of the chelates can be quantitatively extracted in the form of their chloride or acetate salts by a single equilibration with a small portion of isopentanol. The following are only partially extractable: iron(II) chelates of **III** and **IX**; copper(I) chelates of **X**, **XXVIII**, **XXIX** and **XXX**; and cobalt(II) chelates of **VII**, **X**, **XXVIII** and **XXXI**.

Spectral characteristics are summarized in Table I. The wavelengths given are for maximum absorbance unless otherwise specified, and the molar absorptivity values (ε) correspond to the wavelength cited.

TABLE I.—SPECTRAL CHARACTERISTICS OF THE METAL CHELATES

Chromogen	Iron(II) λ, *nm*	 ε, l.mole^{-1}. mm^{-1}	Copper(I) λ, *nm*	 ε, l.mole^{-1}. mm^{-1}	Cobalt(II) λ, *nm*	 ε, l.mole^{-1}.mm^{-1}
I	†	†	425*	550*	†	†
II	†	†	433*	280*	†	†
III	456	$1{\cdot}15 \times 10^{3}$	450*	123*	425*	980*
IV	†	†	492	700	†	†
V	†	†	463	707	†	†
VI	556	$2{\cdot}32 \times 10^{3}$	465	670	512	290
VII	612	$0{\cdot}840 \times 10^{2}$	510	700	463*	210*
VIII	612	950	472	560	463*	250*
IX	569	$1{\cdot}95 \times 10^{3}$	487	550	462*	210*
X	605	$1{\cdot}78 \times 10^{3}$	505*	680*	†	†
XI	558	$2{\cdot}31 \times 10^{3}$	484	550	463*	48*
XII	564	$2{\cdot}33 \times 10^{3}$	496	590	463*	130*
XIII	565	$2{\cdot}44 \times 10^{3}$	490	710	450*	50*
XIV	606	180	437*	96*	412*	$2{\cdot}10 \times 10^{3}$*
XV	447	250	400*	99*	387*	120*
XVI	656	420	450*	137	475*	235*
XVII	425*	89*	437*	55*	412*	52*
XVIII	654	$1{\cdot}19 \times 10^{3}$	400*	84*	400*	300*
XIX	472	490	†	†	†	†
XX	609	810	462*	180*	†	†
XXI	453	350	450*	44*	†	†
XXII	†	†	493	370	†	†
XXIII	†	†	397	490	†	†
XXIV	572	$1{\cdot}45 \times 10^{3}$	412*	120*	515	196
XXV	678	790	453	380	500*	90*
XXVI	542	840	533	700	500*	220*
XXVII	‡	‡	‡	‡	‡	‡
XXVIII	681	780	625*	330*	†	†
XXIX	675	780	612*	160*	†	†
XXX	‡	‡	‡	‡	‡	‡
XXXI	553	$1{\cdot}85 \times 10^{3}$	475	604	500*	240*
XXXII	563	$1{\cdot}87 \times 10^{3}$	455	890	560	170

* Wavelength not a maximum but at shoulder or side of band just before reagent blank absorbance is appreciable.

† Colours and spectra of chelate and chromogen are very similar.

‡ Chromogen not sufficiently soluble for testing.

The most sensitive chromogens of the group for iron are the substituted 1,2,4-triazine derivatives **VI**, **XI**, **XII** and **XIII**. Yielding iron(II) chelates with high molar absorptivities and extractabilities, these chromogens compare favourably in analytical utility with such outstanding reagents as bathophenanthroline,[5] 2,4,6-tripyridyl-*sym*-triazine[6] and 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine.[7]

Compound **XXXII** forms the most intensely coloured copper(I) complex of those studied; however, its reactivity with cobalt(II) and iron(II) seriously detracts from its possible analytical use. Less sensitivity but greater selectivity is afforded by the more stereo-selective chromogens **IV** and **V**. Popular use of any of these, however, is improbable because of the availability of equally selective but more sensitive copper chromogens—*e.g.*, bathocuproine.[8]

The most sensitive cobalt chromogen of the group is the benzimidazole derivative **XIV**. Its analytical utility appears promising, although limited by the necessity of making absorbance measurements on the long wavelength side of an absorption band having its maximum in the ultraviolet. Measurement at shorter wavelengths or at the maximum is precluded by the intense absorption by excess of uncomplexed chromogen. Absorbance interferences from copper, iron and nickel constitute another disadvantage.

The metal–ligand ratios and conditional formation constants of certain of the iron(II) chelates are of interest with regard to structural features of the ligands. Pertinent data are given in Table II. An especially interesting finding is that both **VII** and **VIII** behave as bidentate rather than terdentate ligands in chelation with iron(II). Both possess multiple ferroin groupings with sufficient versatility to act conceivably either as bi- or terdentate ligands. Since the latter mode should lead to greater

TABLE II.—MOLE RATIOS AND CONDITIONAL FORMATION CONSTANTS OF THE IRON(II) CHELATES

Chromogen	Fe:L	Log K*
VII	1:3	6·3
VIII	1:3	6·3
IX	1:3	13
X	1:3	14
XI	1:3	9·3
XII	1:3	9·3
XIII	1:3	9·5
XIV	1:3	10·4
XV	1:3	9·3
XXIV	1:2	15·2

* Based upon measurements of $5 \times 10^{-5}M$ solutions of the complexes in 65% aqueous ethanol, 0·08M in ammonium acetate and 0·02M in hydroxylamine hydrochloride.

stability, it is surprising that these ligands co-ordinate preferentially in the bidentate mode. Apparently the terdentate mode is sterically discouraged by the bulky methyl (or phenyl) group adjacent to the nitrogen atom in the substituted pyridyl ring. Steric hindrance of this type was first observed by Stephen[9] in a comparative study of some pyridyl substituted pyrazines. The most reasonable conclusion is that co-ordination of VII or VIII to iron involves the nitrogen atom of the pyridyl ring at position 6 and the nitrogen in position 1 of the triazine ring.

Another surprising observation is that both IX and X prefer a bidentate to a terdentate mode in chelation of iron(II). Similar to VII and VIII, these ligands have multiple ferroin groupings that should permit either bi- or terdentate co-ordination; but, unlike VII and VIII, no significant steric hindrance should be associated with the terdentate mode. The preferred bidentate action of the ligands, therefore, may be presumed to arise from differences in co-ordinating strengths or electron densities of the various nitrogen atoms. Since one of the nitrogen atoms in the triazine ring must be involved, it is more reasonable to conclude that it is the one in positions 1 or 2 rather than 4. If so, then the ligand has no other choice but to assume a bidentate mode, using either the nitrogen in the isoquinolyl or the pyridyl ring to complete the chelation. Which of these two is utilized is suggested by a comparison of the formation constants and spectral characteristics of the iron(II) chelates of VII, VIII, IX and X. Although closely related, the properties of the chelates are grossly dissimilar. This suggests that the nitrogen of the isoquinolyl ring is involved in chelation with IX and X and that of the unsubstituted pyridyl ring in chelation with VII and VIII.

Nothing unexpected is evident for the chelates of XI, XII, XIII, XIV, XV and XXIV. The results in Table II are consistent with the ligand structures.

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Summary—The chromogenic reactions with iron(II), copper(I) and cobalt(II) of 32 recently synthesized pyridazines, triazines, tetrazines and certain other compounds containing the ferroin grouping have been examined spectrophotometrically. Some interesting examples were found of steric and donor-atom selectivities in chelation of iron by ligands containing several ferroin groups. Of the various chromogens studied, the pyridyl and isoquinolyl derivatives of phenyl or pyridyl substituted 1,2,4-triazine show the most promising analytical utility.

Zusammenfassung—Die farbbildenden Reaktionen von 32 neu synthetisierten Pyridazinen, Triazinen, Tetrazinen und anderen die Ferroingruppe enthaltenden Verbindungen mit Eisen(II), Kupfer(I) und Kobalt(II) wurden spektrophotometrisch untersucht. Einige interessante Beispiele sterischer Selektivität und Auswahl des Donoratoms bei der Chelatbildung von Eisen mit mehrere Ferroingruppen enthaltenden Liganden wurden gefunden. Von den verschiedenen untersuchten Farbreagentien versprechen die Pyridyl- und Isochinolylderivate von phenyl- oder pyridylsubstituiertein 1,2,4-Triazin den größten analytischen Nutzen.

Résumé—On a examiné spectrophotométriquement les réactions chromogènes avec les fer(II), cuivre(I), et cobalt(II) de 32 pyridazines, triazines, tétrazines et certains autres composés contenant le groupement ferroïne, récemment synthétisés. On a trouvé quelques exemples intéressants de sélectivités stériques et de donneurs d'atome dans la chélation du fer par des ligands contenant plusieurs groupes ferroïne. Des divers chromogènes étudiés, les dérivés pyridyl et isoquinolyl de la 1,2,4-triazine phényl ou pyridyl substituée montrent l'utilité analytique la plus prometteuse.

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Determination of alumina in sintered aluminium powder by activation with 14-MeV neutrons*

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S.A.P. (sintered aluminium powder) is a sinter of alumina in an aluminium matrix. The alumina content varies from 4 to 14%. The mechanical and physical properties, and the possible applications, depend largely on the dispersion of the alumina in the matrix.

In this work, we describe the determination of the homogeneity and content of the alumina in extruded S.A.P. bars.

The conventional chemical determination of alumina in S.A.P. is not very suitable, as special apparatus is necessary and the operational time is very long. On the other hand, as neutron-activation analysis is very quick for the determination of oxygen in some materials, it is convenient to use it for the indirect evaluation of alumina in S.A.P. by determination of the oxygen content.

The fast neutron reaction $^{16}O(n, p)^{16}N$ is widely used[2–5] because there are easily operated small neutron generators which produce neutrons of 14-MeV energy. The cross-section of this reaction with 14-MeV neutrons is between 35 and 40 mbarn, which is suitable for our purpose. Furthermore there are very few interferences in the reaction and in the subsequent measurement of the induced ^{16}N activity and only a short time is required to reach saturation activity. This reaction also gives the possibility of counting highly energetic beta-particles and gamma-radiation, because the ^{16}N decays with a half-life of 7·14 sec by beta-emission of 10·4 MeV (26%) to the fundamental state of ^{16}O 4·26

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MeV (68%) in coincidence with 0·14-MeV gamma-radiation and 3·28 MeV (5%) in coincidence with 7·2-MeV gamma-radiation. Both beta and gamma radiations are able to pass through a common aluminium crystal mount.

This technique of oxygen analysis is specific with most samples but, if interferences are present, it is possible to eliminate them by an absorption screen for beta-radiation[4] and a high discrimination level for gamma-radiation.[5-7] It is also possible to use a multichannel analyser. The principal interfering species to eliminate are fluorine, boron, sulphur, aluminium, magnesium, silver and others which give short-lived nuclides. Fluorine and boron are among the most difficult to eliminate.

EXPERIMENTAL

Equipment and reagents

Fast neutrons of 14-MeV energy were produced by the T(d, n)^{4}He reaction in the IMICAM-CISE 150-kV generator.[6]

Figure 1 shows a block diagram of the neutron generator, pneumatic system and counting equipment.

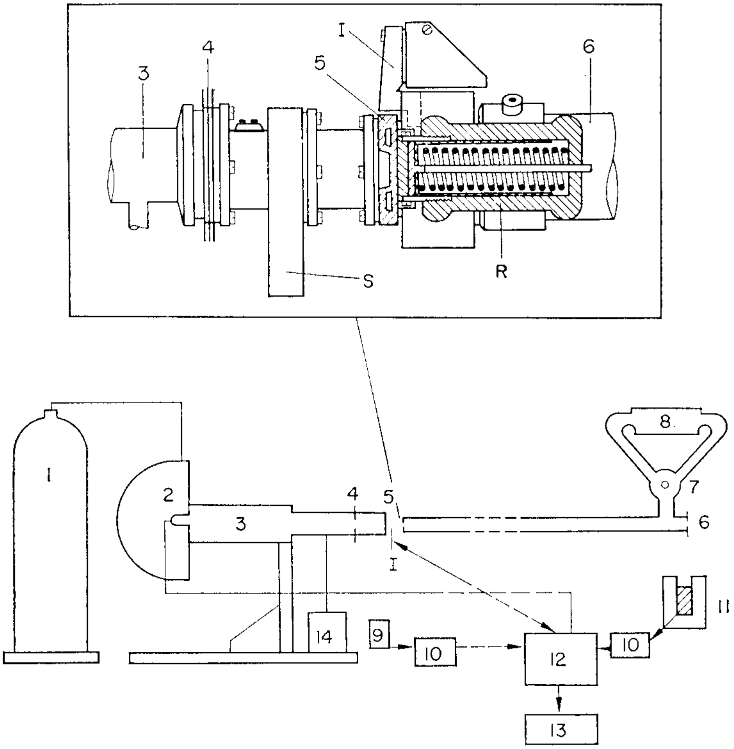

FIG. 1.—Installation scheme.

1—High voltage; *2*—ion source; *3*—accelerator tube; *4*—focussing electrode; *5*—tritium target support; *6*—pneumatic tube; *7*—valve; *8*—compressor; *9*—Hornyak crystal; *10*—amplifiers; *11*—counting unit; *12*—programmer; *13*—neutron counter; *14*—vacuum pumps; *I*—switch; *R*—rabbit. The upper diagram shows a detail of the target zone.

The high voltage source (1) is a Cockroft-Walton system. The ion source (2), of radio frequency type, with an axial magnetic field, is situated in the generator pillow. Between the high voltage pillow and the accelerator tube (3), which is horizontal, there is only one intermediate electrode, used for the electrostatic focussing of the deuteron beam. An additional electrode (4), at the end of the tube, intercepts the external corona of the deuteron beam, and the ionic current collected gives information on how good the focus is.

To prevent unnecessary use of the target, at the end of irradiation a switch (5) sends a signal which causes introduction of a screen *s* in the path of the deuteron beam, and reduces to zero, by a variable transformer, the voltage applied to the ion source.

A titanium–tritium target (0·062 Ci/mm^2) is mounted on a support that has annular refrigeration. It is used to obtain a neutron flux of 10^5 n.mm^{-2}.sec^{-1} by the T(d, n)^{4}He reaction.

The fast-neutron flux was monitored continuously with a Hornyak crystal[9] at a fixed distance from the target, where the reading could be assumed proportional to the neutron production rate.

Transfer of the sample to the flux zone and from there to the counter is *via* a pneumatic tube system (6), because of the short half-life of ^{16}N. This is done by reversing the air-flow by means of a reverse flow valve (7) which inverts the compressor flow (8).

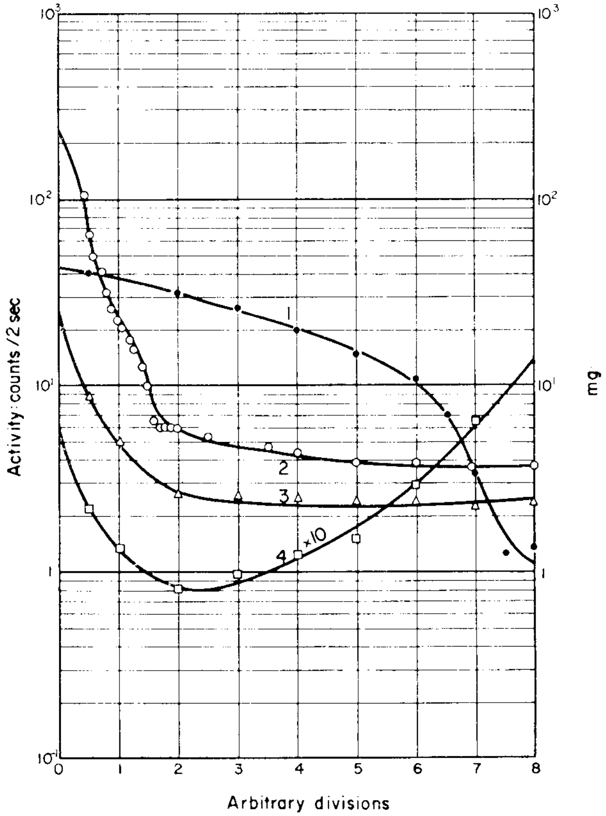

FIG. 2.—Determination of the sensitivity.
1—^{16}N activity which corresponds to 1 mg of oxygen; *2*—background activity (*b*); *3*—minimum number of counts detectable; $n_e = 0{\cdot}26\,[1 + \sqrt{(1 + 14b)}]$; *4*—sensitivity in mg.

A programmer system (12) allows the automatic realization, by means of a switch signal, of the following steps: confirmation of correct sample positions, neutron counting during the irradiation time, and automatic interruption of neutron flux at the end of irradiation. The samples must be introduced in a reproducible way, behind the neutron source; the sample is situated in the centre of the head of a rabbit by means of an adjustable ring.

The rabbit consists of a polyethylene plastic cylinder 0·20 m long with a diameter of 70 mm. Because of the high-gradient neutron flux in the neighbourhood of the source, there is a thin stainless-steel dismountable window in the head of the rabbit. A piston with a polyurethane coat compresses the sample against the window. A full length spring is axially located in the cylinder, in order to absorb the collision impact when the rabbit strikes the source. The rabbit head operates, *via* a switch *I*, a red light to indicate correct positioning of the sample. The counting system consists of a 75 × 75 mm NaI(Tl) crystal and is in optical contact with a "Dumond" multiplier phototube.

Pulses from the phototube are fed to a preamplifier and model AMZ linear amplifier with a discrimination threshold between 0·2 and 4·2 V, and a model CT6 scaler and a unit measuring a prefixed time. All of these were constructed in the Electronic Laboratory of CCR Euratom Ispra. An Olivetti ST2 punch is also used.

Procedure

Irradiation. Individual samples were irradiated for 30 sec and transferred to the NaI(Tl) detector by the pneumatic system in approximately 10 sec. The generator was operated at a deuteron beam current of 200 μA, and accelerating voltage of 125 kV and with a 4-Ci titanium–tritium target.

The determination of the flux was not necessary because a chemically analysed reference S.A.P. standard and a nylon standard were used.

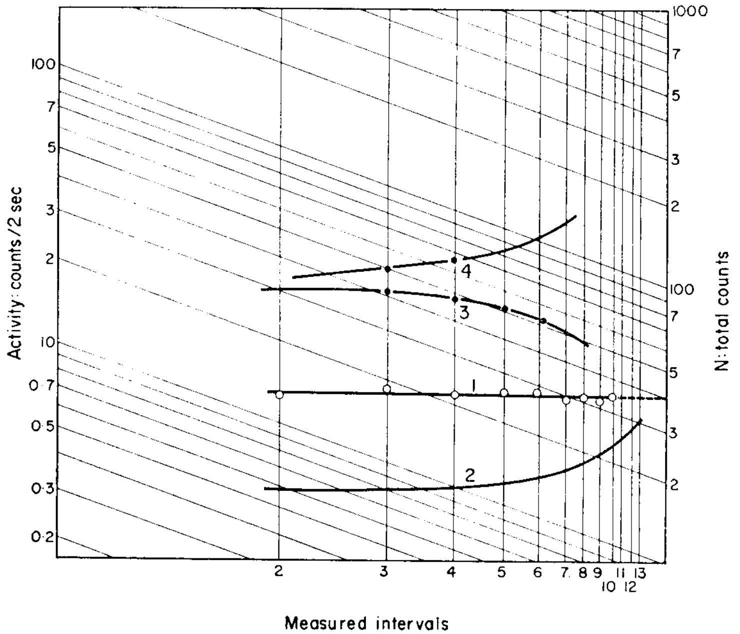

FIG. 3.—Graphic construction for the evaluation of total ^{16}N activity. *1*—Total activity of a pure ^{16}N source (experimental); *2*—total activity of ^{16}N and another activity of $t_{1/2} = 20$ sec; *3*—total activity of a radioisotope of $t_{1/2} = 5$ sec; *4*—total activity of a radioisotope of $t_{1/2} = 10$ sec. Values from reference (6).

The samples and the standard were cylinders 10 mm long and 10 mm in diameter. Both solid samples were placed in the axis of the rabbit head. No containers were used; therefore no problems arose due to oxygen in the containers.

Counting. An irradiation of 2 min and an immediate multichannel counting shows that the fast neutron reactions ^{27}Al(n, p)^{27}Mg, ^{27}Al(n, α)^{24}Na, ^{27}Al(n, γ)^{28}Al with the aluminium of the matrix are the principal interferences. A discrimination of 5·5 arbitrary divisions was used to eliminate them. To avoid the contribution of the oxygen activity from the rabbit materials or of the air in the vessel, the samples are removed from the counter by the operator and inserted by hand in a prefixed place above the crystal with a plastic guide.

Measurement of the ^{16}N was made by counting all the pulses with energy above 3 MeV for 10 intervals of 2 sec in 2π geometry. In these conditions the sensitivity of the method for oxygen determination is 0·2 mg. Figure 2 shows sensitivity *vs.* discrimination level.

The accuracy of the oxygen determination depends on the determination of the ^{16}N activity. Because the source has a short life and quickly arrives at background activity, the optimum counting time is necessarily short for determination of the integral activity of nitrogen-16.

The total sample activity is determined by Girardi and Pauly's graphical integral method. In the nomogram shown in Fig. 3 the accumulated activity value is plotted for each interval $p = 2$ sec. In this form a line parallel to the x axis is obtained. The extrapolated value gives the total number of counts *N* produced from the beginning of counting. The plot of our measurements produces a horizontal line, meaning that only ^{16}N is counted. In fact, the curves which belong to radioisotopes of different half-life and which are also plotted do not give a horizontal line and can be easily discarded. Even mixtures with ^{16}N give a line which is not horizontal.

RESULTS

The results were normalized to a 10^4 neutron flux and for a 10-sec count. When a nylon standard was used the effect of the self-absorption of the nitrogen-16 gamma rays of the samples was neglected. This correction was less than the error limits of the method for the range of samples and standards used.

In Tables I and II are shown the results obtained with a known S.A.P. standard and a nylon standard with a content of 106 mg of oxygen.

TABLE I.—Al_2O_3 CONTENT OF S.A.P., MEASURED *vs.* STANDARD S.A.P. (4% Al_2O_3)

Sample	Weight *g*	No. of determinations	Mean Al_2O_3 %	Mean error, % Al_2O_3
FF 23 C	2·154	10	$4{\cdot}2_6$	$0{\cdot}1_3$
FF 24 T	2·132	10	$4{\cdot}7_4$	$0{\cdot}1_4$
FF 24 C	2·131	10	$4{\cdot}3_1$	$0{\cdot}1_8$
FF 20 C	2·177	6	10·9	$0{\cdot}9_0$
FF 20 T	2·192	6	$10{\cdot}1_6$	$0{\cdot}4_8$

Sample FF 23 T is taken as reference standard, containing 4·0% of Al_2O_3; T and C denote the top and bottom of a 2-m extruded bar.

TABLE II.—Al_2O_3 CONTENT OF S.A.P. MEASURED *vs.* NYLON STANDARD (106 mg OF OXYGEN)

Sample	Weight *g*	No. of determinations	Mean Al_2O_3 %	Mean error, % Al_2O_3
FF 23 T	2·030	22	$3{\cdot}6_5$	$0{\cdot}1_0$
FF 23 C	2·154	12	$3{\cdot}7_4$	$0{\cdot}1_2$
FF 24 T	2·132	11	$4{\cdot}0_4$	$0{\cdot}1_2$
FF 24 C	2·131	10	$3{\cdot}7_2$	$0{\cdot}1_6$
FF 20 C	2·177	9	$9{\cdot}1_3$	$0{\cdot}3_5$
FF 20 T	2·192	15	$9{\cdot}5_5$	$0{\cdot}3_2$

The results obtained show that at the higher levels of oxygen content in S.A.P. (2–7%) the relative mean error of the method is approximately 5%. Chemical analysis gives a better precision but nevertheless is very complicated and slow.

The difference between the results obtained with nylon or S.A.P. standards can be explained by their different neutron dispersion.

The high flux gradient present in the irradiation geometry can be a source of error if the position of samples and comparison standard are not exactly reproduced, especially with thick samples. It is possible to overcome this error by the use of internal monitoring of the neutron flux. As an example, we used the aluminium of the matrix as an internal flux monitor. By the reaction $^{27}Al(n, p)^{27}Mg$, aluminium is activated to ^{27}Mg of 8·9 min half-life. Gamma-rays of 0·84 and 1·02 MeV are emitted. The specific activity of ^{27}Mg, at zero time, is proportional to the incident neutron flux. Measurements of the ^{27}Mg were made with 5 counts at intervals of 1 min, in the same geometrical conditions, the first of them 2 min after the end of irradiation.

Now with the use of the internal flux monitoring standard we indeed obtain a better precision. For sample FF23C a mean value of 3·83% of Al_2O_3 content was obtained, with a mean relative error of 2% for 12 determinations. In this case the precision is increased but so is the analysis time. For this reason the external standard method was used for the other samples.

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Summary—Fast neutrons of 14 MeV produced in the IMICAM CISE 150-kV generator by the (d, t) reaction in a tritium-titanium target, were used in the indirect determination of Al_2O_3. The samples were irradiated for 30 sec and the total ^{16}N activity was determined, by counting for ten 2-sec periods and graphically integrating. The standards were a known sintered aluminium powder and nylon pieces of identical shape. The method is competitive with the chemical one, because of its quickness, sensitivity and precision.

Zusammenfassung—Schnelle Neutronen von 14 MeV, die im IMICAM CISE 150 kV-Generator durch (d, t)-Reaktion in einem Tritium-Titan-Target erzeugt wurden, fanden Anwendung bei der indirekten Bestimmung von Al_2O_3. Die Proben wurden 30 sec bestrahlt und die gesamte ^{16}N-Aktivität durch Zählen über zehn 2 sec-Abschnitte und graphische Integration bestimmt. Als Standards dienten ein bakanntes gesintertes Aluminium-pulver und Nylonstücke von identischer Form. Das Analysenverfahren kann wegen seiner Geschwindigkeit, Empfindlichkeit und Genauigkeit mit dem chemischen in Konkurrenz treten.

Résumé—On a utilisé les électrons rapides de 14 MeV produits dans le générateur de 150 kV IMICAM CISE par la réaction (d, t) dans une cible tritium-titane dans le dosage indirect de Al_2O_3. Les échantillons ont été irradiés pendant 30 s et l'on a déterminé l'activité totale 16N, en comptant pendant dix périodes de 2 s et en intégrant. Les étalons étaient une poudre d'aluminium fritté connue et des morceaux de nylon de même forme. La méthode est concurrentielle avec la méthode chimique, à cause de ses rapidité, sensibilité et précision.

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The role of solution equilibria in atomic-absorption spectroscopy: P. E. Thomas and W. F. Pickering. (4 *May* 1970)

Solvent extraction of metal–Alizarin Red S chelates in the presence of 1,3-diphenylguanidium salts—I. Indium(III)–Alizarin Red S system: Makoto Otomo and Koichi Tonosaki. (6 *May* 1970)

Polarographic behaviour of cadmium, lead, nickel, thallium and uranium(VI) in isoquinoline formate: A. L. J. Rao and B. K. Puri. (12 *May* 1970)

Titration curves in complexometric titrations with the Fe^{3+}/Fe^{2+} redox system: Adam Hulanicki and Regina Karwowska. (12 *May* 1970)

Determination of zinc in food—a comparative study: M. L. Higgins and W. F. Pickering. (13 *May* 1970)

Oxidation of hydrazine with Chloramine-T: V. R. S. Rao. (15 *May* 1970)

Microdetermination of nitrates and nitrites—III. Gasometric and gravimetric methods based on reduction with formic acid: W. I. Awad, S. S. M. Hassan and M. R. M. Zaki. (15 *May* 1970)

Selektive Bestimmung in verdünter Lösung befindlicher Säuren von verschiedener Stärke durch oszillometrische Titration: Zs. Szabó-Ákos and L. Erdey. (19 *May* 1970)

Investigation of alkali metal and ammonium tetraphenylborates by infrared spectrophotometry. Determination of ammonium ions in the presence of alkali metal ions: K. Kiss-Eröss, I. Buzás and L. Erdey. (19 *May* 1970)

Use of complex displacement reactions in photometric analysis: J. Inczédy. (19 *May* 1970)

Talanta, 1970. Vol. 17, p. iii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Dissociation Constants of Inorganic Acids and Bases in Aqueous Solution: D. D. PERRIN. Butterworths, London, 1969. Pp. 103. 44s.

This is the third volume of a series prepared at the request of the Commission on Electrochemical Data of IUPAC (and is therefore published as part of *Pure and Applied Chemistry*, 1969, Vol. 20). Over 200 compounds (including hydrolysable metal ions) are listed with as much information as is necessary to appreciate the usefulness of the data. The literature has been covered up to 1967. The author points out that this collection aims to cover only pK_a and pK_b values. and the reader is referred to *Stability Constants* (Sillén and Martell) for other equilibrium constants Not only research workers in inorganic and physical chemistry, but also teachers of the latter in search of data for problems will find this a valuable and useful handbook.

Gas Chromatography: L. SZEPESY (English trans. ed. E. D. MORGAN). Iliffe, London, 1970. Pp. 8 + 384. 100s.

This is a further addition to the substantial number of texts dealing with gas chromatography. This example has a very complete introductory section outlining the theory of the technique and this is followed by an exhaustive description of the apparatus construction. There are sections describing the qualitative and quantitative applications of gas chromatography to analytical chemistry and an excellent account of the use of the method in process control. Some more unusual applications detailed here include those of elemental analysis and the determination of surface area. This is a text which can be recommended to third year undergraduates, research workers and the analytical chemist in industry.

Practical Manual of Gas Chromatography: ed. JEAN TRANCHANT. Elsevier, London, 1969. Pp. XIX + 387.

This is the English translation of the second French Edition of the manual. It collects together a body of factual material concerned with the purely empirical aspects of gas chromatography. There are chapters dealing with both qualitative and quantitative analysis with the gas chromatograph and a section describing other applications of the technique. There are over eight hundred references to the literature and the text is profusely illustrated.

Enzymatic Methods of Analysis: GEORGE G. GUILBAULT. Pergamon Press, Oxford, 1970. Pp. xv + 347. 75s.

This book introduces the reader to the subject of enzymes and the methods used for following the kinetics of enzyme reactions. Then follow chapters dealing with the determination of Enzymes, Substrates, Activators and Coenzymes, and Inhibitors. The last two chapters discuss the Immobilized Enzyme (which has simplified the production and marketing of enzymes) and the use of Automation in Enzymic Analysis. This is a field of rapidly growing interest to analysts, particularly since equipment designed for following the kinetics of reactions automatically is commercially available, and this book should provide a useful and readable guide for anyone interested in trace analysis. Printed by offset-litho, it is not as lengthy as its 347 pages would suggest, but the literature coverage up to 1968 is good.

Talanta, 1970, Vol. 17, p. iv. Pergamon Press. Printed in Northern Ireland

ERRATUM

In the paper by A. Townshend and A. Vaughan, *Talanta*, 1970, **17**, 289, in Table III, the amounts of zinc taken and found should be in *ng*, not *μg*.

Talanta. 1970. Vol. 17, p. v. Pergamon Press. Printed in Northern Ireland

NOTICE

3RD ROMANIAN NATIONAL CONFERENCE ON ANALYTICAL CHEMISTRY

The Chemistry Department of the Romanian National Council of Engineers and Technicians will sponsor the 3rd National Conference on Analytical Chemistry between 22 and 26 September 1971 in Brașov, Romania.

The following sessions are planned.

A. Electrometric methods
B. Optical methods
C. Separation methods.

Further information on this meeting is available from the secretary: Dr. Constantin Luca, Consiliul Național al Inginerilor și Tehnicienilor, Conferinta de Chimie Analitică, Calea Victoriei 118, București, Romania.

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SUMMARIES FOR CARD INDEXES

Komplexe der Anthranil-*N*,*N*-diessigsäure mit Metallen in der Oxydationsstufe +4—I. Zirkonium und Hafnium: C. Drăgalescu, Septimia Policec and T. Simonescu, *Talanta*, 1970, **17,** 557. (Academia Republicii Socialiste Romania, Baza de Cercetări Stiintifice, Timişoara, Blv. Mihai Viteazul 24, Romania.)

Summary—Spectrophotometric studies have shown that zirconium and hafnium form complexes with anthranil-*N*,*N*-diacetic acid (ANDA) in aqueous solution, with the compositions Me:ANDA 1:1 and 1:2. The conditional stepwise formation constants at pH 1 were found to be $k_1 = 20 \pm 5$ and $k_2 = 1{\cdot}42 \times 10^5$ for zirconium, and $k_1 = 10 \pm 5$ and $k_2 = 1{\cdot}22 \times 10^6$ for hafnium.

Gleichzeitige spektrophotometrische Bestimmung des Zirkoniums und Hafniums: Septimia Policec, T. Simonescu und C. Drăgulescu, *Talanta*, 1970, **17,** 567. (Academia R.S.R., Baza de Cercetări Stiinţifice, Timişoara, Mihai Viteazul 24, Romania.)

Summary—Zirconium may be determined in the presence of hafnium by ultraviolet spectrophotometry at the isosbestic wavelengths of 218·2, 243·3 or 298·5 nm, with anthranil-*N*,*N*,-diacetic acid in dilute acid solution. Hafnium may be determined in the presence of zirconium from measurements at 216·5, 242·5 or 297 nm. Concentrations in the range 2–36 μg/ml (Zr)and 3–70 μg/ml (Hf) may be determined, and in admixture, from 2·5 to 80% of Zr in Hf, and *vice versa*, with an error of 3–4%.

Analysis by phase titration of three-component systems containing two mutually immiscible components: S. K. Suri, *Talanta*, 1970, **17,** 577. (Chemistry Department, Indian Institute of Technology, New Delhi-29, India.)

Summary—A method, based on phase titration, for the analysis of ternary mixtures containing two mutually immiscible or partially miscible components is described. It can also be used for the determination of tie-lines. The method is illustrated by its application to the system consisting of benzene, cyclohexane and nitromethane.

КОМПЛЕКСЫ АНТРАНИЛ-*N*,*N*-ДИУКСУСНОЙ КИСЛОТЫ С МЕТАЛЛАМИ В СТЕПЕНИ ОКИСЛЕНИЯ +4—I. ЦИРКОНИЙ И ГАФНИЙ:

C. Drăgulescu, Septimia Policec and T. Simonescu, *Talanta*, 1970, **17**, 557.

Резюме—Спектрофотометрические изучения показали что цироконий и гафний образуют комплексы с антранил-*N*,*N*-диуксусной кислотой (АНДК) в водном растворе, состава Me:АНДК = 1:1 и 1:2. Обусловленные ступенчатые константы образования при pH 1 равны $\kappa_1 = 20 \pm 5$ и $\kappa_2 = 1,42 \times 10^5$ для циркония, и $\kappa_1 = 10 \pm 5$ и $\kappa_2 = 1,22 \times 10^5$ для гафния.

ОДНОВРЕМЕННОЕ ОПРЕДЕЛЕНИЕ ЦИРКОНИЯ И ГАФНИЯ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ:

Septimia Policec, T. Simonescu and D. Drăgulescu, *Talanta*, 1970, **17**, 567.

Резюме—Цирконий определен в присутствии гафния методом ултрафиолетовой спектрофотометрии при изозбестических длинах волн 218,2, 243,5 или 298,5 нм, с антранил-*N*,*N*-диуксусной кислотой в разбавленных растворах кислот. Гафний определяют в присутствии циркония измерением светопоглощения при 216,5, 242,5 или 297 нм. Метод позволяет определять 2–36 мкг/мл Zr и 3–70 мкг/мл Hf, а всмеси—2,5–80 % Zr в Hf и обратно, с ошибкой равной 3–4 %.

АНАЛИЗ МЕТОДОМ ФАЗОВОЙ ТИТРАЦИИ ТРЕХКОМПОНЕНТНЫХ СИСТЕМ СОДЕРЖАЩИХ ДВА НЕРАСТВОРИМЫХ ОДИН В ДРУГОМУ КОМПОНЕНТА:

S. K. Suri, *Talanta*, 1970, **17**, 577.

Резюме—Описан метод, основан на фазовой титрации, для анализа тройных смесей содержащих два нерастворимых или частично растворимых один в другому компонента. Метод применим в определении связывающих линий. Метод иллютсрирован его применением в системе бензол-циклогексан-нитрометан.

Determination of vanadium in refractory metals, steel, cast iron, alloys and silicates by extraction of an NBPHA complex from a sulphuric–hydrofluoric acid medium: ELSIE M. DONALDSON, *Talanta*, 1970, **17**, 583. (Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.)

Summary—A method for determining up to 0·15% of vanadium in high-purity niobium and tantalum metals, cast iron, steel, non-ferrous alloys and silicates is described. The proposed method is based on the extraction of a red vanadium(V)–*N*-benzoyl-*N*-phenylhydroxylamine complex into chloroform from a sulphuric–hydrofluoric acid medium containing excess of ammonium persulphate as oxidant. The molar absorptivity of the complex is 428 $l.mole^{-1}.mm^{-1}$ at 475 nm, the wavelength of maximum absorption. Interference from chromium(VI) and cerium(IV) is eliminated by reduction with iron(II). Common ions, including large amounts of titanium, zirconium, molybdenum and tungsten, do not interfere.

Relative sensitivity of rare earth elements in spark-source mass spectrometry: ELEN ROALDSET, *Talanta*, 1970, **17**, 593. (Institutt for Geologi, University of Oslo, Oslo, Norway.)

Summary—A method for calculating the relative sensitivity factors for the rare earth elements in geological material is outlined. A close correlation is found between the relative sensitivity factors calculated and isotopic mass and the first ionization potential for the elements. The points are grouped in the vicinity of a regression line, which may be used to determine the relative sensitivity factors for all the rare earth elements.

Indirect determination of fluorides by the EDTA titration of samarium: H. F. COMBS and E. L. GROVE, *Talanta*, 1970, **17**, 599. (IIT Research Institute, Chicago, Illinois 60616, U.S.A.)

Summary—Fluorides are determined by the back-titration of excess of samarium with EDTA to the canary yellow end-point of Methylthymol Blue. The fluoride is precipitated and digested in a solution buffered at pH 2·5–3·0 with monochloroacetate buffer. After digestion, the pH is adjusted to 5·6–5·8 with pyridine and the excess of samarium is back-titrated in the presence of the precipitate, for samples with small quantities of fluoride. The procedure was used to analyse simple fluorides, fluoroborates and some other fluoro-complexes.

ОПРЕДЕЛЕНИЕ ВАНАДИЯ В ОГНЕУПОРНЫХ МЕТАЛЛАХ, СТАЛИ, ЧУГУНЕ, СПЛАВАХ И СИЛИКАТАХ ИЗВЛЕЧЕНИЕМ В ФОРМЕ КОМПЛЕКСА С НБФГА ИЗ СЕРНО-ФТОРИСТОВОДОРОДНОКИСЛЫХ СРЕД:

ELSIE M. DONALDSON, *Talanta*, 1970, **17**, 583.

Резюме—Описан метод определения до 0,15% ванадия в высокочистотном металлическом ниобие и тантале, в чугуне, стали, цветных сплавах и силикатах. Метод основан на извлечении красного комплекса ванадия (V) с *N*-бензоил-*N*-фенилгидроксиламином (НБФмА) хлороформом из раствора серной и фтористоводородной кислоты, содержащего избыток персульфата аммония в качестве окислителя. Молярное светопоглощение комплекса равно 428 л.моль$^{-1}$.мм$^{-1}$ при 475 нм, т.е. при длины волн максимума светопоглощения. Влияние хрома(VI) и церия(IV) исключено восстановлением с железом(II). Обыкновенные ионы, включая большие количества титана, циркония, молибдена и вольфрама не мешают определению.

ОТНОСИТЕЛЬНАЯ ЧУВСТВИТЕЛЬНОСТЬ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ В МАСС-СПЕКТРОМЕТРИИ С ИСКРОВЫМ ИСТОЧНИКОМ:

ELEN ROALDSET, *Talanta*, 1970, **17**, 593.

Резюме—Предложен метод вычисления относительных факторов чувствительности для редкоземельных элементов в геологическом материале. Обнаружена строгая функциональная связь между вычисленными относительными факторами чувствительности, массы изотопов, и первым потенциалом ионизации элементов. Точки расположены близко линии регрессии, которой можно пользоваться для определения относительных факторов чувствительности для всех редкоземельных элементов.

КОСВЕННОЕ ОПРЕДЕЛЕНИЕ ФТОРИДОВ ТИТРОВАНИЕМ САМАРИЯ С ЭДТА:

H. F. COMBS and E. L. GROVE, *Talanta*, 1970, **17**, 599.

Резюме—Фторидионы определяют оттитровыванием избытка самария с ЭДТА до светло-желтого конца титрования с метилтимоловым голубим. Фторид осаждают и дигерируют в растворе буфферированном при pH 2,5–3,0 с монохлоруксусным буффером. После дигерирования pH приводят к 5,6–5,8 пиридином и избыток самария титрируют в присутствии осадка в случае небольших количеств фторида. Метод применяли в анализе простих фторидов, борофторидов и некоторых других комплексов фтора.

Influence of pH in fluorescence and phosphorescence spectrometric analysis: S. G. Schulman and J. D. Winefordner, *Talanta*, 1970, **17**, 607. (Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.)

Summary—An account is given of the theory of the effect of pH changes on fluorescence and phosphorescence of organic species which exhibit acid–base properties, and of the practical applications of the effect.

Determination of iridium in mafic rocks by atomic absorption: F. S. Grimaldi and M. M. Schnepfe, *Talanta*, 1970, **17**, 617. (U.S. Geological Survey, Washington, D.C., U.S.A.)

Summary—Iridium is determined in mineralized mafic rocks by atomic absorption after fire-assay concentration into a gold bead. Inter-element interferences in the atomic-absorption determination are removed and Ir sensitivity is increased by buffering the solutions with a mixture of copper and sodium sulphates. Substantial amounts of Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Ni, Pb, Te, Ti, V, Y, Zn and platinum metals can be tolerated in the atomic-absorption determination. The sensitivity and detection limits are 3·2 and 0·25 ppm of Ir, respectively.

Studies on nucleation from solution of some analytically important metal chelates: J. A. Velazquez and O. E. Hileman Jr, *Talanta*, 1970, **17**, 623. (Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.)

Summary—The combination of precipitation from homogeneous solution and Vonnegut's droplet technique is employed in the study of nucleation from solution of bis(1,2-cyclohexanedionedioximato)-Ni(II), bis(1,2-cycloheptanedionedioximato)Ni(II), bis(1,2-cyclohexanedionedioximato)Pd(II) and bis(1,2-cycloheptanedionedioximato)-Pd(II). Values of the kinetic constant, surface energy, critical radius and the number of molecules per critical nucleus are calculated and discussed in terms of the limitations of the classical theory of nucleation when applied to crystal nucleation from aqueous solutions of electrolytes.

ВЛИЯНИЕ pH В АНАЛИЗЕ МЕТОДАМИ ФЛУОРЕСЦЕНТНОЙ И ФОСФОРЕСЦЕНТНОЙ СПЕКТРОМЕТРИИ:

S. G. Schulman and J. D. Winefordner, *Talanta*, 1970, **17**, 607.

Резюме—Обсуждена теория влияния перемен pH на флуоресценцию и фосфоресценцию органических соединений, обладающих кислотно-щелочными характеристиками, и применение этого эффекта в практике.

ОПРЕДЕЛЕНИЕ ИРИДИЯ В МАФИЧЕСКИХ ГОРНЫХ ПОРОДАХ МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОМЕТРИИ:

F. S. Grimaldi and M. M. Schnepfe, *Talanta*, 1970, **17**, 617.

Резюме—Иридий определен в минерализованных мафических горных породах методом атодом атомно-абсорбционной спектрометрии после концентрирования в перле золота сухим путем. Межэлементные влияния в определении методом атомно-абсорбционной спектрометрии исключены и чувствительность метода для Ir повышена буфферированием растворов смесью сульфатов меди и натрия. Значительные количества Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Ni, Pb, Te, Ti, V, Y, Zn, и платиновых металлов можно толерировать в определении методом атомно-абсорбционной спектрометрии. Чувствительность и предел обнаружения равны 3,2 и 0,25 мкг/л Ir, соответственно.

ИЗУЧЕНИЕ НУКЛЕАЦИИ ИЗ РАСТВОРОВ НЕКОТОРЫХ ВАЖНЫХ ДЛЯ АНАЛИТИЧЕСКОЙ ХИМИИ ХЕЛАТОВ МЕТАЛЛОВ:

J. A. Velazquez and O. E. Hileman, *Talanta*, 1970, **17**, 623.

Резюме—Использована комбинация осаждения из гомогенного раствора и методакапель Воннегута для изучения нуклеации из раствора бис(1,2-циклогександион-диоксимато)Ni(II) бис(1,2-циклогептандион-диоксимато)Ni(II), бис-(1,2-циклогександион-диоксимато)Pd(II) и бис(1,2-циклогептандион-диоксимато)Pd(II). Вычислены значения кинетической константы, поверхностной энергии, критического радия и числа молекул в критическом ядре и обсуждены в свете ограничений классической теории нуклеации, при мененной в нуклеации кристаллов из водных растворыо электролитов.

Determination of carbon monoxide in metal carbonyl complexes—II. Development of a volumetric finish: A. D. CAMPBELL and P. E. NELSON, *Talanta*, 1970, **17**, 633. (Department of Chemistry, University of Otago, Dunedin, New Zealand.)

Summary—The method previously described for the determination of carbon monoxide in metal carbonyl complexes has been modified to provide an accurate volumetric finish.

Contributions to the analytical chemistry of osmium and ruthenium—IX. The dimercapto derivatives of asymmetric triazine as colour reagents for osmium: GR. POPA, C. LAZAR and C. CRISTESCU, *Talanta*, 1970, **17**, 635. (Laboratory for Analytical Chemistry of the Chemical Faculty, University of Bucharest, Romania.)

Summary—The parameters of the reaction of osmium with 3,5-dimercapto-6-(ethylcarboxy)-1,2,4-triazine have been studied and the optimum conditions for the spectrophotometric determination of osmium over the range 0·5–18·0 ppm determined. The coloured product contains the components in the ratio 1:2, metal:ligand.

Submicro determination of aluminium, bismuth and copper in organometallic compounds: R. BELCHER, BARBARA CROSSLAND and T. R. F. W. FENNELL, *Talanta*, 1970, **17**, 639. (Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham 15, U.K., and Royal Aircraft Establishment, Farnborough, Hants., U.K.)

Summary—Methods for the determination of aluminium, bismuth and copper in samples of organometallic compounds weighing 40–110 μg have been developed. Spectrophotometric determination following digestion with nitric and sulphuric acids in a sealed tube is recommended, all results obtained from the analysis of standard compounds being within ±0·3% absolute error. Digestion in an open tube with perchloric and sulphuric acids gives satisfactory results for bismuth compounds but erratic and often low results for aluminium and copper compounds.

ОПРЕДЕЛЕНИЕ ОКИСИ УГЛЕРОДА В МЕТАЛЛОКАРБОНИЛНЫХ КОМПЛЕКСАХ—II. РАЗРАБОТКА ВОЛУМЕТРИЧЕСКОГО МЕТОДА ИЗМЕРЕНИЯ:

A. D. Campbell and P. E. Nelson, *Talanta*, 1970, **17**, 633.

Резюме—Раньше описанный метод определения окиси углерода в металлокарбонилных комплексах изменен включением точного волуметрического метода измерения.

ВКЛАД В АНАЛИТИЧЕСКУЮ ХИМИЮ ОСМИЯ И РУТЕНИЯ—IX. ДИМЕРКАПТОПРОИЗВОДНЫЕ АСИММЕТРИЧЕСКОГО ТРИАЗИНА В КАЧЕСТВЕ ЦВЕТНЫХ РЕАГЕНТОВ ДЛЯ ОСМИЯ:

Gr. Popa, C. Lazar and C. Cristescu, *Talanta*, 1970, **17**, 635.

Резюме—Изучены параметры реакции осмия с 3,5-димеркапто-6-(этилкарбокси)-1,2,4-триазином и определены оптимальные условия для спектрофотометрического определения осмия в области концентраций 0,5–18,0 частей на миллион. Отношение металла и лиганда в окращенном продукте равно 1:2.

СУБМИКРООПРЕДЕЛЕНИЕ АЛЮМИНИЯ, ВИСМУТА И МЕДЫ В ОРГАНОМЕТАЛЛИЧЕСКИХ СОЕДИНЕНИЯХ:

R. Belcher, Barbara Crossland and T. R. F. W. Fennell, *Talanta*, 1970, **17**, 639.

Резюме—Разработаны методы определения алюминия, висмута или меди в образцах органометаллических соединений 40–110 мкг. Предложено спектрофотометрическое определение после дигерирования азотной или серной кислотами в запаянной трубке. Вси результаты полученные в анализе эталонов имели ошибку меньше чем ±0,3 % абс. Дигерирование в открытой трубке с хлорной и серной кислотами дает удовлетворительные результаты для соединений висмута, но ошибочные и часто низкие результаты для соединений алюминия и меди.

Fällung des Wismuts als Bis(triphenylselenonium)-Pentachlorobismutat(III): Max Ziegler und Lüder Ziegeler, *Talanta*, 1970, **17**, 641. (Anorganisch-Chemisches Institut, der Universität, Göttingen, Deutschland.)

Summary—By precipitation as $[(C_6H_5)_3Se]_2[BiCl_6]$ in the presence of citrate, 15–50 mg of bismuth can be determined gravimetrically, and separated from moderate amounts of bi- and tervalent metals and from phosphate. Such metals can be identified by the formation of the triphenylselenonium salts of their various halide complexes.

Two new spectrophotometric reagents for copper: Lawrence Stookey, *Talanta*, 1970, **17**, 644. (Hach Chemical Company, P.O. Box 907, 713 South Duff, Ames, Iowa 50010, U.S.A.)

Summary—Two ferroin-type compounds are proposed as spectrophotometric reagents for copper(I): 6-methyl-2-pyridylhydrazidine, which forms a yellow complex with λ_{max} 426 nm and molar absorptivity 700 $l.mole^{-1}.mm^{-1}$, and 3-(6-methyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine, which forms a red-orange complex with λ_{max} 492 nm and molar absorptivity of 955 $l.mole^{-1}.mm^{-1}$. These reagents are specific for copper and the complexes can be extracted into isopentanol for increased sensitivity.

Amperometric titration of Cd(II), Hg(II) and Zn(II) in molten alkali thiocyanates with electrolytically generated sulphide ions: Paolo Cescon, Filippo Pucciarelli and Mario Fiorani, *Talanta*, 1970, **17**, 647. (Istituto Chimico dell'Università di Camerino, Camerino, Italy.)

Summary—The feasibility of the titration of some cations in molten sodium thiocyanate–potassium thiocyanate mixture with electrolytically generated sulphide ions has been tested at 443 K. Quantitative data are given for the titration of cadmium, mercury and zinc ions.

ОСАЖДЕНИЕ ВИСМУТА В ФОРМЕ БИС(ТРИФЕНИЛСЕЛЕНОНИЙ)-ПЕНТАХЛОРОВИСМУТАТА(III):

Max Ziegler and Lüder Ziegeler, *Talanta*, 1970, **17**, 641.

Резюме—15–50 мг висмута определено весовым методом осаждением в форме $[(C_6H_5)_3Se]_2[BiCl_5]$ в присутствии цитрата, и отделено от умеренных количеств дву- и трехвалентных металлов и от фосфата. Эти металлы отождествлены образованием солей трифенилселенония их разных галоидкомплексов.

ДВА НОВЫХ СПЕКТРОФОТОМЕТРИЧЕСКИХ РЕАГЕНТА ДЛЯ МЕДИ:

Lawrence Stookey, *Talanta*, 1970, **17**, 644.

Резюме—Предложены два соединения типа ферроина в качестве реагентов для меди(I): 6-метил-2-пиридилгидразидин, образующий желтый комплекс с $\lambda_{\text{макс}}$ 426 нм и молярным светопоглощением 700 л.моль$^{-1}$.мм$^{-1}$, и 3-(6-метил-2-пиридил)-5,6-дифенил-1,2,4-триазин, который образует красно-оранжевый комплекс с $\lambda_{\text{макс}}$ 492 нм и молярным светопоглощением 955 л.моль$^{-1}$.мм$^{-1}$. Реагенты являются специфическим для меди, а комплексы извлекаемы изопентанолом для повышения чувствительности.

АМПЕРОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ Cd, Hg(II) И Zn В РАСПЛАВЛЕННЫХ ТИОЦИАНАТАХ ЩЕЛОЧНЫХ МЕТАЛЛОВ С ЭЛЕКТРОЛИТИЧЕСКИМ ПУТОМ ОБРАЗОВАННЫМИ СУЛЬФИДИОНАМИ:

Paolo Cescon, Filippo Pucciarelli and Mario Fiorani, *Talanta*, 1970, **17**, 647.

Резюме—Испытана возможность титрования некоторых катионов в расплавленной смесе тиоцианатов натрия и калия при 443° К с электролитическим путом образованными сульфидионами Приведены количественные данные для титрации кадмия, ртути и цинка.

New chromogens of the ferroin type—VI. Some derivatives of 1- and 3-cyanoisoquinoline and substituted 2-cyanopyridines: Alfred A. Schilt, Wayne E. Dunbar, Bruce W. Gandrud and Steven E. Warren, *Talanta*, 1970, **17**, 649. (Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.)

Summary—The chromogenic reactions with iron(II), copper(I) and cobalt(II) of 32 recently synthesized pyridazines, triazines, tetrazines and certain other compounds containing the ferroin grouping have been examined spectrophotometrically. Some interesting examples were found of steric and donor-atom selectivities in chelation of iron by ligands containing several ferroin groups. Of the various chromogens studied, the pyridyl and isoquinolyl derivatives of phenyl or pyridyl substituted 1,2,4-triazine show the most promising analytical utility.

Determination of alumina in sintered aluminium powder by activation with 14-MeV neutrons: Carlos E. Español and Ana María Marafuschi, *Talanta*, 1970, **17**, 653. (Facultad de Ingeniería, Universidad de Buenos Aires, Argentina.)

Summary—Fast neutrons of 14 MeV produced in the IMICAM CISE 150-kV generator by the (d, t) reaction in a tritium-titanium target, were used in the indirect determination of Al_2O_3. The samples were irradiated for 30 sec and the total ^{16}N activity was determined, by counting for ten 2-sec periods and graphically integrating. The standards were a known sintered aluminium powder and nylon pieces of identical shape. The method is competitive with the chemical one, because of its quickness, sensitivity and precision.

НОВЫЕ ХРОМОГЕНЫ ТИПА ФЕРРОИНА—VI. НЕКОТОРЫЕ ПРОИЗВОДНЫЕ 1- И 3-ЦИАНОИЗОХИНОЛИНА И ЗАМЕЩЕННЫХ 2-ЦИАНОПИРИДИНОВ:

Alfred A. Schilt, Wayne E. Dunbar, Bruce W. Gandrud and Steven E. Warren, *Talanta*, 1970, **17**, 649.

Резюме—Изучены спектрофотометрическим методом хромогенные реакции с железом(II), медью(I) и кобальтом(II) 32 новоситезированных пиридазинов, триазинов, тетразинов и некоторых других соединений содержащих ферроингруппу. Обнаружены интересные примеры стерической селективности и селективности на основе атома-донора в хелатообразовании с железом лигандов содержащих несколько ферроингрупп. Из исследованных хромогенов пиридил- и изохинолилпроизводные фенил- или пиридилзамещенного 1,2,4-триазина оказались наиболее полезными для применения в анализе.

ОПРЕДЕЛЕНИЕ ОКИСИ АЛЮМИНИЯ В СПЕКШЕМСЯ ПОРОШКОВИДНОМ АЛЮМИНИЕ АКТИВАЦИЕЙ С 14-МЭВ НЕЙТРОНАМИ:

Carlos E. Español and Ana Maria Marafuschi, *Talanta*, 1970, **17**, 653.

Резюме—Быстрые нейтроны произведенные в 150 кв генераторе IMICAM CISE реакцией (d, t) в щите трития-титана использованы для косвенного определения Al_2O_3. Образци облучены в течение 30 сек. и определена общая ^{16}N активность, считанием в 10 периодов по 2 сек. и графическим интегрированием. Знакомые образци спекшегося порошковидного алюминия и образци найлона той же формы служили в качестве эталонов. Метод сравным с химическим методом по его быстроты, чувствительности и точности.

Photochemistry and Photobiology

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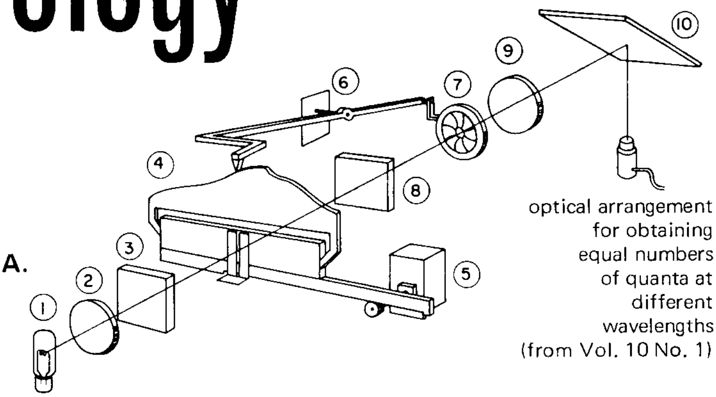

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