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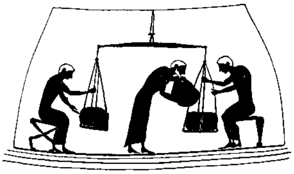

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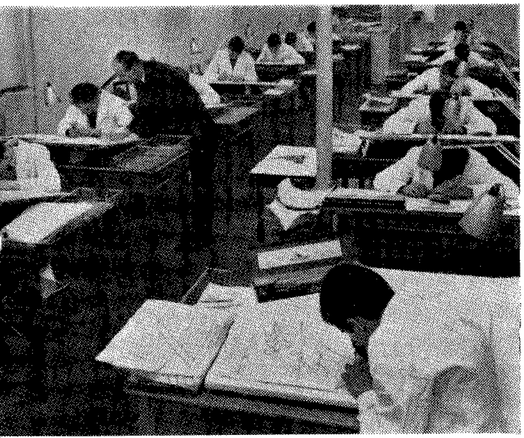

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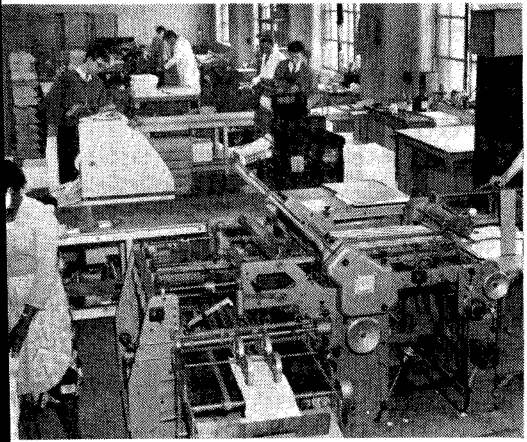

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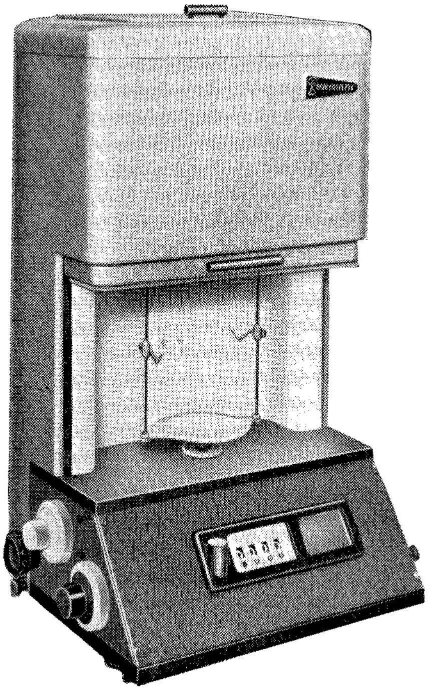

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FIG. 1. A. STEYERMARK (U.S.A.), Chairman of the Committee for the **International Symposium on Microchemical Techniques,** 13–18 August, 1961, organised by the Metropolitan Microchemical Society under the sponsorship of I.U.P.A.C., welcomes participants at the first Plenary Session.

FIG. 2. Speakers at one of the Technical Sessions of the Symposium (left to right): A. M. TROZZOLO (U.S.A.), A. LACOURT (Belgium), H. WALDMANN (Switzerland), M. BRANDSTÄTTER-KUHNERT (Austria), A. KOFLER (Austria) and W. C. MCCRONE (U.S.A.).

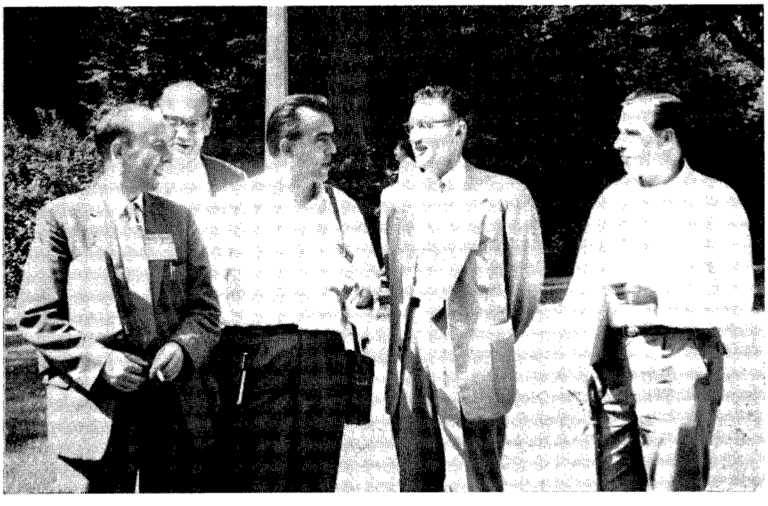

FIG. 3. A group on the campus of Pennsylvania State University, U.S.A., where the Symposium was held (left to right): G. INGRAM (U.K.), H. MALISSA (Austria), W. SCHÖNIGER (Switzerland), C. L. OGG (U.S.A.) and S. HÖLZL (Austria).

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DIE BESTIMMUNG KLEINER FLUORMENGEN—I

EINE KRITISCHE ÜBERSICHT

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Zusammenfassung—Eine kritische Studie, in welcher festgestellt wird, daß bei den verschiedenen Typen der Fluorbestimmung sowohl mit als auch ohne Trennung im Prinzip dieselben Komponenten stören. Eine Gleichung, welche die Verhältnisse bei der destillativen Fluorabtrennung wiedergibt, wurde abgeleitet und mit veröffentlichten, experimentellen Resultaten verglichen. Die Literaturangaben sind nur selten älter als aus dem Jahre 1955.

DIE Bedeutung der Fluorbestimmung ist vielseitig. In Trink-und Mineralwässern und weiter in der Luft, hauptsächlich von Aluminium- bzw. Fluorwerken, ist es aus gesundheitlichen Gründen notwendig, den Fluorgehalt zu verfolgen. Da die Grenzen des hygienisch unbedenklichen Fluorverbrauches manchmal sehr eng angegeben werden (1,3–1,5 mg pro Tag),[1] müssen die Bestimmungen genau durchgeführt werden. In der Hydrogeologie beurteilt man nach der Fluoridkonzentration die Genese mancher Thermalwässer und in der Archäologie das Alter der Knochen nach der Relation ihres Fluorgehaltes zu ihrem Phosphatgehalt. In der Industrie, organischen Chemie und Physiologie ist es z.B. notwendig, Fluorverunreinigungen im Aluminium, das unter Zusatz von Kryolith hergestellt wird, oder Fluor in einer Reihe bedeutender organischer Verbindungen (Freone, Teflon, "Nerven"-Gifte, usw.) zu bestimmen.

In natürlichen Materialien und hauptsächlich in Mineralwässern kann das Fluor in einigen Formen vorkommen, nämlich als Fluorid, Fluoaluminat, Fluoferrat, Fluosilikat, Fluoborat usw. Deshalb muß man vor allem seinen Gesamtgehalt bestimmen, welcher meistens ungenau als "Fluoridgehalt" bezeichnet wird. Diese Arbeit gibt eine kritische Übersicht der diesbezüglichen analytischen Methoden. In der Zukunft wird es jedoch notwendig sein, auch einzelne Existenzformen des Fluors zu bestimmen, denn es erscheint von vornherein nicht ausgeschlossen, daß der physiologische Einfluß von Fluorid ein anderer ist als der von stabilen Fluorsystemen.

Die Bestimmung kleiner Fluormengen wird gegenwärtig meistens spektralphotometrisch und photometrisch durchgeführt. Zu diesem Zweck nützt man vor allem die entfärbende Wirkung der Fluoride auf Farblacke und -chelate von mehrwertigen Kationen mit organischen Farbstoffen aus. Die Entfärbung anorganischer Komplexe ist weniger günstig. Immer wieder studiert man die Lacke von Alizarin S, in diesem Zusammenhang gewöhnlich nur als Alizarin bezeichnet,[2–5] von Purpurin-Sulfat[6] mit Zirkonium und von Alizarin S mit Thorium;[7,8] neuerdings finden auch folgende Kombinationen Anwendung: Chromazurol S,[9] Amarath,[10] Thoron[11] bzw. Phenylfluoron,[13] Neothorin[12] mit Thorium; Eriochromcyanin R,[14–19] Brenzkatechinviolett,[20] SPADNS,[21] weniger gebräuchliche Farbstoffe[22,23] und in letzter Zeit Xylenolorange[109] mit Zirkonium; Aluminon,[24] Haematoxylin,[25] Chromazurol S[26,27] bzw. Eriochromcyanin R[27,28] mit Aluminium; Salicylsäure,[29] Antipyrin[30] und eine Reihe anderer Reagentien[31] mit Eisen(III); Chromotrosäure,[32] Phenylfluoron[33] und Ascorbinsäure[34] mit Titan und schließlich Chromazurol S mit Beryllium.[35]

Weiterhin werden auch schwerlösliche Verbindungen herangezogen, die bei der Reaktion mit Fluorid eine photometrierbare Komponente freigeben, z.B. Lanthan-[36] und Thoriumchloranilat[37] oder Zirkonium-4-Dimethylaminoazobenzol-4-arsenat.[38] Man benutzt auch den Inhibitoreinfluß der Fluoride auf die Phosphatase und photometriert das freigewordene Phosphat[39,40] bzw. die katalytische Redoxreaktion zwischen Ce(III) und Ce(IV) Ionen.[41] Die einzige bekannte Farbreaktion mit Fluorid ermöglicht eine Lösung von Cer(III)-3-aminomethylalizarin-N,N-Diacetat, welche für qualitative[42] und mit ungleichem Erfolg für quantitative[43,110,119] Zwecke benutzen kann, siehe auch.[110] Fluorometrische Fluorbestimmungen lassen sich mit den Aluminiumchelaten von Oxychinolin oder Morin,[44] Eriochromarot B bzw. Superchrom Garnet Y[45] ausführen. Niedrige Fluorgehalte werden auch herkömmlich volumetrisch bestimmt, und zwar mit visueller,[46,47] photometrischer,[48,49] fluorometrischer,[50] turbidimetrischer,[51] potentrimetrischer,[52] amperometrischer,[53–55] konduktometrischer,[56,57] Hochfrequenz-[58,59] bzw. radiometrischer[60] Indikation. Neulich gebrauchte man eine coulometrische[111] und dead-stop[112] Titration.

Man titriert in der Regel mit Lösungen derselben Kationen, welche bei den photometrischen Bestimmungen gebraucht werden. Bei visueller Endpunktsanzeige verwendet man auch meistens dieselben Farbstoffe.

Zu polarographischen Bestimmungen nützt man polarographisch aktive Chelate oder Komplexe mit verschiedenen der erwähnten Kationen aus, z.B. mit Aluminium[61] oder Eisen,[62] und inaktive Chelate, z.B. mit Thorium, welche aktive Stoffe freigeben.[63] Man verwendete auch die innere Elektrolyse mit einer Zirkonelektrode.[64]

Die Empfindlichkeit der angewendeten chemischen Fluorbestimmungen ist nicht nur von den Eigenschaften der mit dem Fluorion reagierenden Komplexe (von ihrer Farbintensität usw.) im Zusammenhang mit einer guten Indikation des Reaktionsablaufs abhängig, sondern auch von den stöchiometrischen Verhältnissen in den entstehenden Verbindungen. In diesen kann das Verhältnis Fluor zu Kation sehr verschieden sein; in der Literatur wird 6, 4, 2 bis 1:1 angegeben. Es entstehen z.B. TiF_6^{2-}, ThF_4,[55], $ZrOF_2$,[4] FeF^{2+} [30] und $TiOF^+$.[32]

Bei den chemischen Fluorbestimmungen, die sich eigentlich nur auf einige sehr verschiedenartig verfolgte Grundreaktionen stützen, werden die Resultate stets mehr oder weniger durch Anionen erhöht, die ähnliche Eigenschaften wie das Fluorion besitzen. Es sind dies hauptsächlich Phosphate (welche praktisch bei allen Bestimmungen stören), Sulfate (welche bei Gebrauch von Zirkon, Thorium, Lanthan, Cer und manchmal auch Eisen und Titan stören), bzw. auch Arsenate, Borate, Chloride usw. Höhere Resultate werden auch durch Oxydationsmittel, z.B. Chlor, verursacht, welche die benutzten organischen Stoffe zersetzen. Negative Fehler können auftreten, indem das Fluorion durch Aluminium-, Eisen(III) Ionen bzw. Kieselsäure getarnt wird, oder z.B. Eisen(III)- bzw. Manganionen mit dem angewandten Farbstoff unerwünschte Chelate bilden.

Bei dem Gebrauch von Cer(III)-aminomethylalisarin-N,N-Diacetat wird ein Fehler von 10% z.B. bei einem 650maligem Sulfat und 0,3maligem Aluminium-Ionen Überschuß verursacht.[110] Beim Gebrauch von Zr-Xylenolorange beträgt nach vorläufigen Angaben[109] der Fehler eines 5maligen Aluminium-Ionen Überschusses 0% und eines 1000maligen Sulfat Überschusses 12%; bei entsprechenderen Bedingungen, welche später veröffentlicht werden, stört auch ein 3–5 Tausendmaliger Überschuß von Sulfaten nicht.

Wenn man in der Methode,[42] in welcher Belcher und Mitarbeiter das erste mal einen Farbstoff mit einer di(carboxymethyl)-amino-methyl Gruppe zur Bestimmung von Fluor ausnützten, anstatt die Cer(III)-Ione diejenigen von Zirkonium gebrauchen möchte, würde man mit größter Wahrscheinlichkeit ähnliche Resultate wie mit Xylenolorange bekommen (log der Stabilitätskonstanten von CeF^{2+} und ZrF^{3+} sind 3,11 und 8,71[75]). Da die Konstante von CeF^{2+} markant kleiner als die von AlF^{2+} (6,13) und FeF^{2+} (5,17) und größer als die von CaF^{+} (0,51) und MgF^{+} (1,30) ist und da bei der Methode[42,110] Sulfate und Phosphate nicht beträcht lich stören, könnte man sie mit Vorteil zur Bestimmung des freien bzw. wenig stabil gebundenen Fluors in vielen Wässern gebrauchen. Den Einfluß von Ca-Ionen, welcher sich nach experimentellen Angaben[110] schon von einem 10maligem Überschuß anoffenbart, wird man mittels Korrektionsnomogramme eliminieren müssen. Das auf diese Weise bestimmte Fluor könnte dem biologisch aktiven Fluor entsprechen—man kann sich nämlich vorstellen, daß z.B. das Fluor, welches die Atmung der Pflanzen vermindert,[120] das die Enolase aktivierende Magnesium tarnt, welches die Respiration erhöht.

Aus höher angeführten Gründen ist es deshalb sehr vorteilhaft, in manchen Materialien, besonders in Aluminium, den Fluorgehalt spektrographisch auf Grund der Molekularbande von CaF und SrF zu bestimmen.[65,66] im metallischen Zirkonium wird er in Heliumatmosphäre mittels der Atomlinien von Fluor oder besser des Molekülbandsystems von Zirkoniumfluorid[113] bestimmt. Zur aktivierungsanalytischen Bestimmung von Fluor wurde die mit thermischen Neutronen induzierte Aktivität des Isotops ^{20}F (Halbwertszeit- 11 sec.)[67] oder die durch schnelle Neutronen hervorgerufene Aktivität des Isotops ^{16}N (7,6 sec.)[68] benutzt. Die hofnungsvollste Reaktion $^{19}F(n, 2n)^{18}F$ (112 min., Empfindlichkeit 0,1 μg F)[114] wird sicher auch bald analytisch ausgenützt werden. Vor kurzem nützte man auch die nukleare magnetische Resonanz[115] aus.

Da bei der Bestimmung des Fluor-Gesamtgehaltes eine Anzahl von Komponenten stört, versuchte man immer dessen Abtrennung. Am gebräuchlichsten ist hierzu das schon klassische Destillationsverfahren (s. Offermann 1890). Ihm wird deshalb hier besondere Aufmerksamkeit gewidment.

In welcher Form das Fluor destilliert, ist z.B. in den Arbeiten [69,70] beschrieben.

Bei dem überwiegenden Destillationstyp[71] kann man das Fluor von einer etwa äquimolaren Menge von Zirkonium überhaupt nicht trennen.[72] Aus dem Milieu einer konzentrierten Aluminium-Lösung ist die Geschwindigkeit der Fluorabtrennung eine im Prinzip logarithmische Funktion der Zeit[70] und wird bei einem annähernd hundertfachen Aluminium-Überschuß praktisch Null. Weiter fanden Rennert und Mitarbeiter[73] bei der Destillation aus 1 g Pflanzenmaterial 30 ppm F und aus 10 g derselben Probe 7 ppm F; z.B. in 1 und 5 g desselben Grases wurden 44 und 35 ppm F gefunden.[74] Ein ähnlicher Effekt, welcher bei der Bestimmung von Fluor ohne Abtrennung von Aluminium beobachtet wurde, wird später angeführt.

Die Ursache der erwähnten Schwierigkeiten liegt in der Abhängigkeit des Partialdruckes des abzudestillierenden Fluorwasserstoffes über der Lösung von seiner

Konzentration in der Lösung, welche ihrerseits eine Funktion der Stabilitätskonstanten der entsprechenden Fluorsysteme und der Konzentration aller Kationen, Silikate und Borate in der Lösung ist. Da die Stabilität der Fluorsysteme, insbesondere von Zirkonium und auch von Aluminium, außerordentlich hoch ist,[75] sind die Fehler, welche durch die Anwesenheit dieser Elemente im zu analysierenden Material verursacht werden, sehr markant. Die Resultate der Arbeiten[73,74] rühren davon her, daß bei größeren Einwaagen die Komponenten, welche Fluorsysteme bilden, infolge ihrer erhöhten Konzentration in der Destillationslösung das Fluor stärker binden und seinen abdestillierbaren Anteil herabsetzen.

Quantitativ kann obige Erklärung für die Unvollkommenheiten der destillativen Fluorabtrennung durch die im weiteren Text abgeleitete Gleichung wiedergegeben werden:

$$s_F = S_F(1 - e^{-kAt}) \tag{1}$$

Hierin bedeuten S_F die ursprünglich vorhandene und s_F die zur Zeit t abdestillierte Fluormenge.

Die Gleichung folgt aus der allgemeinen Geschwindigkeitsgleichung 1. Ordnung für die Destillation von Flußsäure

$$-\frac{d_{CHF}}{dt} = k \,.\, C_{HF} \tag{2}$$

wobei sich C_{HF} mit C_F^- und C_{MF} im Gleichgewicht befindet. MF ist die einfachste Form eines Metallion-Fluorion-Systems in der Lösung, das die destillative Fluorabtrennung stört.

$$C_{HF} = K_{HF} \,.\, C_{H^+} \,.\, C_{F^-} = K_{HF} \,.\, C_{H^+} \,.\, K_{MF}{}^{-1} \,.\, C_{M^+}{}^{-1} \,.\, C_{MF} \tag{3}$$

K_{HF} und K_{MF} sind die Stabilitätskonstanten der Flußsäure bzw. des Fluorion-Metallion-Systems. Im allgemeinen Fall, bei dem in der Lösung m MF bis MF_n Systeme vorliegen, lautet der Ausdruck

$$C_{HF} = K_{HF} \,.\, C_{H^+} \sum_m \left(\sum_{n=1}^{n} K_{MF_n}^{-1} \,.\, C_{MF_{n-1}}^{-1} \,.\, C_{MF_n} \right)_m \tag{3a}$$

Bei in der Wirklichkeit vorkommenden hohen Konzentrationen der Säure und anderer Komponenten der Lösung, aus welcher destilliert wird, muß man auch deren Aktivitätskoefizienten in Betracht nehmen. Es soll jedoch nur ein einziges System MF betrachtet werden. Für den praktisch wichtigen Fall $C_{M^+} \gg C_{MF}$ läßtsich schreiben

$$C_{HF} = B \,.\, C_{MF} \quad \text{wobei} \quad B = K_{HF} \,.\, C_{H^+} \,.\, K_{MF}{}^{-1} \,.\, C_{M^+}{}^{-1} \tag{4}$$

Da im betrachteten Beispiel das Fluor als Fluorwasserstoff abdestilliert wird, gilt in Gleichung (2) die Identität

$$-\frac{dC_{HF}}{dt} \equiv -\frac{dC_F}{dt} \tag{5}$$

C_F ist die Fluor-Totalkonzentration in Lösung.

$$C_F = C_{HF} + C_{MF} + C_{F^-} = A^{-1} \,.\, C_{HF}$$

$$\text{wobei} \quad A^{-1} = 1 + B^{-1} + K_{HF}^{-1} \,.\, C_{H^+}^{-1} \text{ und } A = \frac{K_{HF} \,.\, C_{H^+}}{K_{HF} \cdot C_{H^+} + K_{MF} \cdot C_{M^+} + 1} \tag{6}$$

Wenn $K_{MF} . C_{M^+} \gg 1 + K_{HF} . C_{H^+}$, dann $A = K_{HF} . C_{H^+} . K_{MF}^{-1} . C_{M^+}^{-1} = B$ und wenn $K_{MF} . C_{M^+} + 1 \ll K_{HF} . C_{H^+}$, dann $A = 1$.
Somit geht Gleichung (2) in den Ausdruck

$$-\frac{dC_F}{dt} = k . A . C_F \tag{7}$$

über. Integration in den Grenzen $t = 0$ bis t liefert

$$\frac{(C_F)_t}{(C_F)_0} = e^{-kAt} \tag{7a}$$

$(C_F)_t$ ist die zur Zeit t, $(C_F)_0$ die zur Zeit 0 vorhandene Fluor-Totalkonzentration in der Lösung. Der Konzentrationsverlust durch Destillation beträgt $(C_F)_0 - (C_F)_t = \frac{s_F}{v}$, wo v das Lösungsvolumen bedeutet. Mit dem entsprechenden Ausdruck $(C_F)_0 = \frac{S_F}{v}$ wird aus Gleichung (7a) schließlich die Gleichung (1) erhalten:

$$s_F = S_F(1 - e^{-kAt})$$

wobei A den Wert von 1 bis $B \ll 1$ hat.

Die Größe k enthält wahrscheinlich nur noch die Abhängigkeit α der Fluorwasserstoffkonzentration C_{HF} in und c_{HF} über der Lösung und experimentelle Parameter, d.h. Werte, welche von der Form der Destillationsapparatur, der Destillationsgeschwindigkeit usw. abhängen. Sie werden in der Größe η zusammengefaßt, die man als quantitatives Maß für die Effektivität der einzelenn veröffentlichten, bis jetzt aber objektiv nicht vergleichbaren Varianten der destillativen Fluorabtrennung benutzen könnte. Im allgemeinen Falle kann die Größe k auch die Geschwindigkeitskonstante k_{MF} des Zerfalles von MF in M^+ und F^- enthalten. Also $k = M\alpha^{-1}k_{MF}$.

Eine vorläufige halbquantitative Bestätigung der angeführten Interpretationen kann in der in letzter Zeit veröffentlichten Arbeit[108] gesehen werden, welche den Destillationsverlauf von Fluor aus einer sauren Lösung von Aluminiumfluorid verfolgt. Aus der Abbildung, in welcher auf der Abszisseder Logarithmus des nicht überdestillierten Fluorgehaltes log $(S_F - s_F)$ und auf der Ordinate die Zeit t aufgetragen wird, ist nämlich ersichtlich, daß der Verlauf des log $(S_F - s_F)$ zuerst durch eine Gerade der Neigung—1,3 wiedergegeben wird, welche nach einer bestimmten Zeit in eine Gerade der Neigung —0,78 und endlich —0,42 übergeht. Nach der oben entwickelten Vorstellung sollten die einzelnen Destillationsgeschwindigkeiten, welche durch ihre Richtungsfaktoren charakterisiert sind, die man als Destillationsgeschwindigkeits-Konstanten bezeichnen könnte, dem nacheinander verlaufenden Zerfall der zunehmend stabileren Systeme AlF_3, AlF_2^+ und AlF^{2+} entsprechen. Die Abhängigkeit, welche durch Vergleich der einzelnen Richtungsfaktoren $K_n = \Delta \log (S_F - s_F)/\Delta t$ mit den Logarithmen der Stabilitätskonstanten der entsprechenden Fluoaluminate (siehe Fig. 1) erhalten wurde, befindet sich nicht im Widerspruch zu den Gleichungen (1) und (2), indem s_F bzw. $-dc_{HF}/dt$ den Stabilitätskonstanten der in der Lösung anwesenden Fluorsysteme indirekt proportional sind. Infolge der Dissoziation der Fluoaluminate, welche bei den weniger stabilen Systemen selbstverständlich größer als bei den festeren ist, entstehen die Knicke der Destillationskurve erst nach dem Überdestillieren von 60 und 82% Fluor. Wenn aber in der Arbeit[108] aus einer Lösung mit Zugabe von Phosphorsäure destilliert wird, welche die Destillation von Fluor im allgemeinen verlangsamt (Entstehung festerer ternärer Aluminium-Fluor-Phosphat-Systeme?), zeigen sich die Knicke in der Destillationskurve nach dem Überdestillieren von 45 und 66% Fluor. Der letzte Knick deutet ziemlich genau auf die Existenz eines Systems mit dem Verhältnis Al:F = 1:1 hin, aus welchem das Fluor infolge geringer Dissoziation nur noch sehr langsam destilliert.

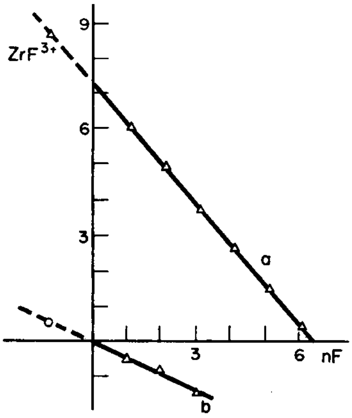

ABB. 1

(*a*) Logarithmen der Stabilitätskonstanten der Fluosysteme $AlF_n^{(3-n)+}$ bei 25°, übernommen aus[75].

(*b*) Werte der Richtungsfaktoren $K_n = \Delta \log (S_F - s_F)/\Delta t$ der einzelnen Abschnitte der Destillationskurve von AlF_3 bei 125°C, übernommen aus[108].

Zu den Werten auf dem gestrichelten Teil der Kurven siehe die Erläuterungen im Text.

Wenn man die Geraden *a* und *b* in Abb. 1 so verlängert, daß man auf *a* ohne Rücksicht auf die Anzahl nF den Logarithmus der Stabilitätskonstante von ZrF^{3+} eintragen kann, so lassen sich auf dem verlängerten Teil der Gerade *b* die Verhältnisse erfassen, welche bei Destillation aus einer ZrF^{3+}-Lösung unter den Bedingungen der Arbeit[108] gelten. Wenn nämlich die Fluordestillation bei sonst konstanten Bedingungen nur um so schwieriger verläuft, je fester Fluor in einem beliebigen System gebunden ist, kann man nicht nur erwarten, daß z.B. die Destillation aus einer Lösung von ZrF_3^+ ($\log K_3 = 5{,}74$)[75] ähnlich verläuft wie aus einer Lösung von AlF^{2+} ($\log K_1 = 6{,}13$), sondern man kann aus dem Verlauf der Destillationsgeschwindigkeits-Konstanten einiger Fluoaluminate in Abhängigkeit von deren Stabilitätskonstanten auch die Werte der Destillationsgeschwindigkeit anderer Systeme abschätzen, sofern deren Stabilitätskonstanten bekannt sind. Aus Abb. 1 geht auf Grund dieser Voraussetzung hervor, daß aus der ZrF^{3+}-Lösung kein Fluor destillieren wird, was mit der Erfahrung übereinstimmt.

Ähnliche Werte könnte man auf Grund desselben Prinzips bekommen, indem man direkt die Kurven der Stabilitätskonstanten und der Destillationsgeschwindigkeits-Konstanten von Zirkonium ableiten würde.

Durch Auswertung einer experimentell und theoretisch gründlicher verfolgten Formulierung der angeführten Gleichung wird man die Grenzen für die Verwendbarkeit der Destillationstrennung von Fluor erfassen und die Fehler dieses "klassischen" Verfahrens unter weniger günstigen Bedingungen bzw. bei früher durchgeführten Analysen abschätzen können.

Besonders wichtig ist es, in der Destillationslösung die höchstzulässigen Konzentrationen an Kalzium und Magnesium festlegen zu können, deren Oxyde organischen und biologischen Analysenproben zur Unterdrückung von Fluorverlusten bei der Veraschung beigemischt werden. Zu hohe Erdalkalizusätze verfälschen die Ergebnisse wahrscheinlich nicht nur absolut, sonder auch relativ. Im Extremfall kännte der nicht überdestillierte Fluor-Anteil im Sinne der Versuche[73,74] bei einem hohen Fluor-Gehalt 0% und bei einem niedrigen Fluor-Gehalt 100% betragen.

Man kann erwarten, daß sich die Faktoren, welche den Verlauf der destillativen Fluorabtrennung beeinflussen, wenigstens im Prinzip auch bei den anderen analytischen Destillationsverfahren durchsetzen werden. Die Ausarbeitung einer Destillationstheorie von Fluor könnte vielleicht einen Anlaß zum Aufbau einer allgemeinen Theorie der analytischen Destillationsverfahren geben.

Die besseren Fluorabtrennungen, welche durch eine Erhöhung der Destillationstemperatur über 135°C erzielt werden, sind von störenden flüchtigen Bestandteilen begleitet. Bei der Destillation aus Perchlorsäurelösungen wird die Säure teilweise zu Chlor reduziert, welches auch schon bei niedrigeren Temperaturen, z.B. durch den Einfluß der Chloride, gebildet werden kann, sofern diese aus der analysierten Lösung nicht entfernt wurden.[1] Bei derDestillation aus Schwefel- bzw. Phosphorsäurelösungen werden demgegenüber nicht vernachlässigbare Mengen von deren Dämpfen abgegeben, weshalb man z.B. ein zweites Mal bei niedrigerer Temperatur destilliert[76] oder das überdestillierte Sulfat fällt.[77]

Da auch die neueren Modifikationen der Fluordestillation[49,73,74,77] nur vorwiegend der organischen Mikroanalyse Verbesserungen bieten, widmet man in der letzten Zeit der Stromdestillation, meist Pyrohydrolyse genannt,[78–83] erhöhte Aufmerksamkeit.

Die Fluorabtrennung wird hier unter Durchleiten von Wasserdampf durch die Probe bei Temperaturen von 600–1000°C in Anwesenheit von Katalysatoren erzielt. Auf diese Art kann man Fluor auch von Zirkonium trennen.[78] Die zur Bestimmung von mg-Mengen günstige pyrohydrolytische Abtrennung kann aber nur schwierig bei der Isolierung von μg-Mengen benutzt werden, welche z.B. in den üblichen analytisch verarbeiteten Volumina von Naturwässern vorhanden sind, da in den gebräuchlichen Apparaturen leicht Verluste des freigesetzten Fluors entstehen. —Bei der sog. Technik der Schönigerflaschen,[84] bei welcher die zu analysierenden Proben in einer Sauerstoff-Wasserstoff-Flamme verbrannt werden,[18,43,85] entstehen noch bei einem Gehalt von 10 mg F Fluorverluste von 10%.[43] Bei den Hochtemperaturtrennungen destillieren schließlich auch einige die Fluordestillation störenden Anionenkomponenten mit über.

Obwohl man durch Pyrohydrolyse auch Fluor von Zirkonium trennen kann, kann man voraussetzen, daß für alle Destillationsverfahren, ebenso wie für das Veraschen oder das alkalische Schmelzen von fluorhaltigen Proben, ähnliche Gleichungen gelten werden, wie die oben angeführten. An die weniger bekannte Existenz von Chelaten bzw. Komplexen bei hohen Temperaturen sei hier nur erinnert. Z.B. ist es üblich, Kalzium bei der flammenphotometrischen Bestimmung der Alkalien mit Hilfe von Phosphat zu tarnen. Auch die schon angeführte spektrographische Bestimmung von Fluor ist nur durch die Stabilität von CaF und SrF oder eines Fluor-Zirconium-Systems im Milieu des elektrischen Bogens möglich.

Es ist zu erwarten, daß die bis jetzt fast völlig vernachlässigte Chemie der Chelate und Komplexe unter extremen Bedingungen von der Fluorchemie neue Impulse erhalten wird.

Die bei den Bestimmungen von mg-Fluormengen störenden Kationen wurden mit Kationenaustauschern im H-[86–91] bzw. Na-Zyklus[92] abgetrennt. Von 1 ppm Fluor kann man mindestens 20fache Überschüsse aller Kationen mit Ausnahme von Zirkonium und Aluminium trennen.[4] Phosphate[93–95] wurden, ebenso wie die EDTA-Komplexe bildenden Kationen[96] von Anionenaustauschern sorbiert. Eine Abtrennung von hohen Sulfatüberschüssen glückte aber weder auf diesem Wege,[97] noch mit einem Kationenaustauscher im Ba-Zyklus.[98] Verschiedenen Autoren gelang es, das Fluor mit einem Kationenaustauscher in Th-Zyklus[99] bzw. mit einem synthetischen Zirkonylsilikat[100] zu isolieren. Die Resultate schwankten jedoch, und die Sorption der Sulfate wurde überhaupt nicht verfolgt. Die Verluste durch Adsorption von Fluor an Glas wurden untersucht[101] und auf Grund dieser eine Isotopenverdünnungsmethode unter Anwendung des Radioisotops F^{18} ausgearbeitet.[102]

Die Isolierung des Fluors durch Extraktion gelang nur aus relativ konzentrierten Lösungen.[103]

Die Mängel der einzelnen Abtrennungsverfahren sind vielleicht am besten aus einer kürzlich veröffentlichten Arbeit[104] ersichtlich: eine Fluormenge von über 2 mg wird erstens pyrohydrolytisch von den Kationen, danach mit einem Anionenaustauscher von den Nitraten und endlich mit einer indirekten Extraktionsbestimmung von den Sulfaten getrennt. Das der Lösung beigemischte Hafnium, welches radioaktives^{181} Hf enthält, wird mit Trioktylphosphin-Oxyd in Hexan extrahiert. Auf Grund der radiometrisch bestimmten Verteilung des Hafniums zwischen den beiden Flüssigkeitsphasen wird dann die Menge des extraktionshemmenden Fluorids durch Vergleich mit einer Standardkurve ermittelt.

Bei der Fluorabtrennung stören also dieselben Komponenten wie bei Fluorbestimmungen ohne vorherige Trennung: Die Komponenten, welche stabile Fluorsysteme bilden, vermindern oder verlangsamen wenigstens die Isolierung bei der Destillation, beim Ionenaustausch und bei der Extraktion. Anionen mit ähnlichen systembildenden Eigenschaften wie Fluoride, hauptsächlich Sulfate, kann man insbesondere durch Ionenaustausch bzw. Pyrohydrolyse nur schwierig trennen. Unter den extremen Bedingungen der Hochtemperaturtrennungen, von denen die Pyrohydrolyse als bestes Verfahren anzusehen ist, findet zwar eine vollständige Freisetzung des Fluors statt, aber es entstehen besonders bei μg-Bestimmungen in der Apparatur relativ hohe Fluorverluste.

Die Trennungsverfahren sind ferner auch deshalb ungünstig, weil sie größere Apparaturansprüche stellen. Deshalb suchte man immer nach Methoden, welche durch Verminderung des größten Störeffektes auch ohne eine Trennung genügend richtige Resultate, wenigstens in einem bestimmten Material, liefern. So kann man niedrige Sulfatüberschüsse bei manchen Verfahren durch genaue Korrekturen mit Hilfe von Nomogrammen berücksichtigen.[14] Bei anderen Methoden vermindert man den Einfluß der Sulfate im Gegenteil durch eine größere Sulfatzugabe zum Fluor Reagens,[2] wobei man die relativ geringe Entfärbungswirkung hoher Sulfatkonzentrationen ausnützt. Verschiedene Autoren vermindern den Sulfat-[46] bzw. Phosphateinfluß[91] durch Zugabe von Kalzium zur Lösung, und andere beseitigen die Sulfate als Bariumsulfat,[15,105] ohne experimentelle Ergebnisse anzugeben. Da man jedoch bei manchen Fluor-Mikrobestimmungen mit dem erwähnten Niederschlag das Bariumfluorid mitreißt,[106] ist es notwendig, die angeführten Verfahren zu überprüfen.

Durch Erhöhung der Farbstoffkonzentration wird die Störwirkung der Phosphate verringert, z.B. bei der Zirkonium-Alizarin-Methode um eine Größenordnung.[3] Dies hängt mit einer Zurückdrüngung der Dissoziation des benutzten Chelats zusammen. Ähnlich wirkt sich auch die Verminderung des pH-Wertes der Lösung aus,[15] wobei auch die Fluoaluminate rascher zersetzt werden.[15]

Die Fluorbestimmung ist bei gleichem relativen Aluminiumüberschuß fehlerhafter bei einer höheren Fluorkonzentration. So werden unter sonst gleichen Bedingungen in 100 ml der Lösungen von 50 μg F neben 50 μg Al noch 44 μg F, von 100 μg F neben 100 μg Al jedoch nur noch 83 μg F gefunden.[2]

Das hängt in ähnlicher Weise, wie bei der Destillation angeführt wurde, mit der größeren Dissoziation der Fluosysteme bei niedrigeren Konzetrationen zusammen. Analog bildet sich bei niedrigen Boratkonzentrationen kein Fluoborat.[107]

Infolge der prinzipiellen und praktischen Unvollkommenheit der "universellen" Trennungsverfahren hat es der Autor für notwendig gehalten, aus den Teilkenntnissen über die Eliminierung der einzelnen Störwirkungen Regeln für die Erforschung praktisch anwendbarer Bestimmungen des Fluor-Gesamtgehaltes ohne Abtrennung zusammenzustellen. Ausführlich werden diese Regeln, welche schon in der Arbeit[109] angedeutet wurden, später veröffentlicht.

Großere Übersichten der älteren Bestimmungen von Fluor sind in den Arbeiten 116–118 enthalten.

Notiz. Eine theoretische und experimentale Studie über die Destillation von Fluor aus komplexbildendendem Milieu wird vorbereitet. Praktisch wird die Destillation hauptsächlich zur Bestimmung von Fluor in Zirkonium-Präparaten ausgenützt. Im Destillationskolben wird Zirkonium mit einem geeignetem Tarnmittel gebunden, dessen einfachste sonts aber weniger geeignete[76,77] Form schon die Schwefel- oder Phosphorsäure ist. Das freigewordene Fluor wird danach aus genügent saurer Lösung abdestilliert und bestimmt. Ähnlicherweise könnte man fluorfreies Zirkonium, Aluminium, usw. zubereiten.

Zu großem Dank bin ich Herrn W. Leonhardt, Dresden verpflichtet, der an der endgültigen Fassung dieser Arbeit beteiligt war.

Summary—In a critical study it is established that in the different types of fluorine determination, with or without prior separation, the same components interfere. An equation is derived which permits the determination of the quantity of fluorine separated during distillation. Values obtained are compared with published results which have been obtained experimentally. Literature references are mainly to material published after 1955.

Résumé—Dans une étude critique, l'auteur établit que dans différents types de dosage du fluor, avec ou sans séparation préalable, les mêmes composés gênent. Une équation en est déduite et permet le dosage de la quantité de fluor séparée pendant la distillation. Les valeurs, obtenues sont comparées- avec les résultats publiés obtenus expérimentalement. Les références de la littérature sont principalement des articles publiés après 1955.

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THE DETERMINATION OF SUB-MICRO QUANTITIES OF THIOL COMPOUNDS

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Summary—A method based on a procedure devised by Saville[1] has been developed for the determination of thiol compounds in alcoholic and hexane solutions at concentrations of 0·0005 to 0·005*M*. The thiol compound is oxidised by bromine water to a sulphonyl bromide which is converted to cyanogen bromide and determined colorimetrically by the method of Aldridge.[2]

INTRODUCTION

A PROCEDURE for determining low concentrations of long chain aliphatic thiols has been developed in order to follow small concentration changes of these compounds when used as dropwise condensation promotors in hexane solution.

Brockhuysen[3] has described a photometric method for this determination, based upon the red colour given by thiols in an alcoholic medium using *N*-ethylmaleimide. Attempts to repeat the work of Brockhuysen were not successful; the optical densities of the coloured solutions were found to reach maximum values very quickly and to remain constant for only a very short time.

Kunkel, Buckley and Gorin[4] have described a method for determining thiols in hydrocarbon solution, in which the thiol is added to a solution of silver dithizonate in carbon tetrachloride. The liberated dithizone is then determined spectrophotometrically. Attempts were made to use this procedure for a number of thiols. Excellent results were obtained using toluene-3, 4-dithiol, but it was not found possible to liberate dithizone when 2-thionaphthol, n-hexane-thiol, dodecane-thiol or octadecane-thiol was used.

Saville[1] has stated that aqueous solutions of thiols, when treated with bromine, give the sulphonyl bromide, which can be converted to cyanogen bromide by reaction with cyanide ions. The cyanogen bromide can then be determined by Aldridge's method,[2] which is based on the von Braun reaction between pyridine and cyanogen bromide to produce an intermediate capable of condensing with benzidine to give a red product. A preliminary examination of the methods for the determination of thiols indicated that the method based upon Aldridge's procedure was the most promising.

EXPERIMENTAL

As a method was required for the determination of thiols in hexane solution, it was necessary to extract one of the reactants (*i.e.* thiol, sulphonyl bromide or cyanogen bromide) from the hexane to a solution so that the colour-producing reaction could be accomplished in an aqueous medium. It was found that isopropyl alcohol was the best solvent for the purpose.

In the first instance Saville's procedure was examined using a solution of n-hexane-thiol in isopropyl alcohol, and possible variations of the reaction conditions were investigated. Finally the procedure was applied to the determination of thiols in hexane solution.

Solutions

n-Hexane-thiol: 1 ml of n-hexane-thiol was dissolved in 250 ml of isopropyl alcohol to give a solution containing approximately 950 μg of SH/ml. From this stock solution, a working solution containing 1–1·5 μg of SH/ml was prepared by dilution with isopropyl alcohol.

Bromine water: 100 ml of water were added to 50 ml of saturated bromine water.

Phenol solution: 2% w/v of phenol and 5% of potassium bromide in water.

Potassium cyanide solution: 0·5% w/v in water.

Aldridge's reagent: Two solutions were prepared:

(*a*) 10 ml of concentrated hydrochloric acid added to 100 ml of constant boiling pyridine/water mixture.

(*b*) 1 g of benzidine hydrochloride dissolved in 20 ml of diluted (2 + 98 v/v) hydrochloric acid.

These two solutions were mixed when required. Any mixed solution unused after 3 days was discarded.

Measurements of optical density were made using either a Hilger and Watts "Spekker" absorptiometer or a Unicam Type SP500 spectrophotometer. Where figures are quoted in the text, the instrument used has also been recorded.

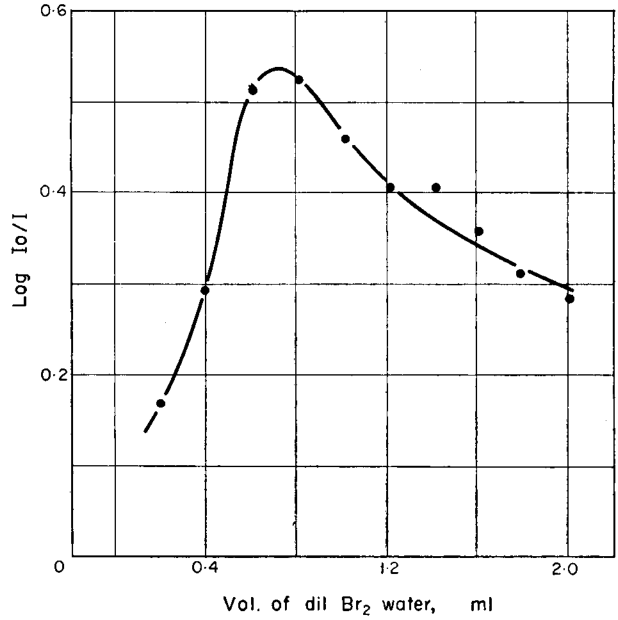

FIG. 1.—Variation of optical density of final solution in relation to the quantity of diluted bromine water used.

Method

One ml of the isopropyl alcohol solution of n-hexane-thiol containing 1–1·5 μg of SH was transferred to a 10-ml measuring flask, 1 ml of diluted bromine water was added, and the flask was shaken; 1 ml of phenol solution was added and the solution was shaken until the colour of bromine had disappeared; then 1 ml of potassium cyanide solution was added, followed by 5 ml of Aldridge's reagent. The optical density of the solution was then measured.

The amount of bromine and reaction time required

The quantity of bromine water used to oxidise the thiol compound was varied between limits of 0·2 and 2 ml, with the remaining conditions as outlined above. The results obtained are shown in Fig. 1.

The maximum value of optical density was given with approximately 0·7 ml of the diluted bromine water. In order to simplify the addition, a new dilution, of 50 ml of saturated bromine water to which

140 ml of water had been added, was prepared. Volumes of 1 ml of this new diluted solution were used for subsequent determinations.

It was noted that low values of optical density were obtained when diluted bromine solutions had been allowed to stand overnight. All such solutions were therefore freshly prepared each day.

It was also noted that if the bromine water was allowed to stand with the thiol reagent for a prolonged period of time, lower values of optical density were recorded. It was therefore necessary to establish the time interval for maximum values of optical density. This was done by using the arbitrary procedure noted above, with a variation of reaction time covering the range 0–14 min. The results obtained are given in Table I.

TABLE I.—VARIATION OF REACTION TIME
Unicam: 525 mμ, 4-cm cells

Reaction time, *min*	0	2	4	6	8	10	12	14
Log I_0/I	0·687	0·687	0·717	0·715	0·713	0·708	0·708	0·702

A reaction time of 5 min was adopted for subsequent work.

Selection of wavelength

Kodak No. 4 filters were used to obtain maximum values of optical density when measurements were made using the Spekker absorptiometer. An absorption spectrum of the red-coloured complex, obtained using the Unicam SP500 spectrophotometer is given in Fig. 2. The maximum absorption was given at a wavelength of 525 mμ.

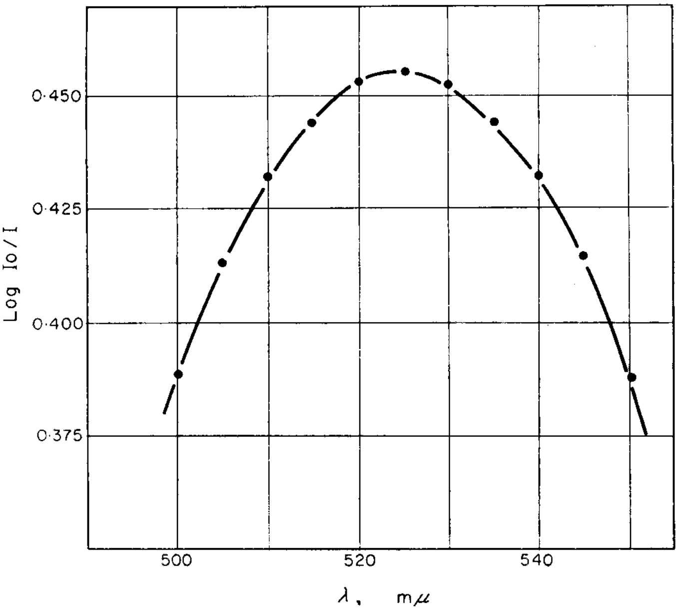

FIG. 2.—Absorption spectrum of the red complex given with Aldridge's reagent.

Variation in volume of sample aliquot

At normal room temperatures, bromine reacts slowly with isopropyl alcohol, and the optical densities obtained with Aldridge's reagent were found to depend upon the volume of alcohol used as solvent. In practice therefore, the volume of the isopropyl alcohol solution was kept at a constant value of 1 ml, and smaller aliquots were diluted to this volume before the addition of the diluted bromine water.

Phenol solution

This solution is added to ensure the complete removal of the excess bromine before adding the potassium cyanide solution. It was found that 5–10 sec, with shaking, was a sufficient time for this reaction to take place, and that increasing this time resulted in low values of optical density, possibly caused by decomposition of the sulphonyl bromide. This is shown in Table II.

TABLE II.—VARIATION OF REACTION TIME FOLLOWING ADDITION OF PHENOL
Spekker: No. 4 filter, 1-cm cell

Reaction time, *sec*	5	10	60	120	180	240
Log I_0/I	0·564	0·564	0·558	0·531	0·523	0·518

Potassium cyanide solution

The cyanide solution reacts with the sulphonyl bromide to give cyanogen bromide. It was observed once again that the optical densities obtained with Aldridge's reagent depended upon the reaction time (Table III).

TABLE III.—VARIATION OF REACTION TIME FOLLOWING ADDITION OF CYANIDE SOLUTION
Unicam: 525 mμ, 2-cm cells

Reaction time, *sec*	10	30	60	120
Log I_0/I	0·250	0·351	0·342	0·214

The addition of Aldridge's reagent

It was noted that the reagent darkened in colour on keeping, but it was shown that for an age of up to 3 days this had no effect upon the final result, the optical density of the reagent blank solution being increased by the same amount as that of the sample solution. For maximum optical density a volume of about 4 ml of Aldridge's reagent was required. With smaller volumes, the colour was not fully developed, and it was difficult to accommodate larger volumes in the measuring flasks used (Table IV).

TABLE IV.—VOLUME OF ALDRIDGE'S REAGENT REQUIRED
Unicam: 524 mμ, 4-cm cells

Vol. of reagent, *ml*	2	3	4	5
Log I_0/I	0·838	0·923	0·936	0·932

On adding Aldridge's reagent to the solution, the red colour rapidly forms and the optical density reaches a maximum value after approximately 20 mins, and then slowly decreases. This is shown in Fig. 3. The optical densities of all coloured solutions were therefore measured 20 min after the addition of Aldridge's reagent.

Thiols in hexane solution

One of the requirements of the method is that the determination of the thiol should be made in hexane solution. As the reaction described does not take place in hexane, it is necessary to transfer one of the reacting species (*i.e.* thiol, sulphonyl bromide or cyanogen bromide) to an aqueous or alcoholic phase.

Attempts were made to evaporate the hexane solvent on a water bath, but in each case attempted, low values of optical density were obtained.

Isopropyl alcohol is miscible with hexane, and attempts were therefore made to produce a homogeneous solution containing hexane, thiol and isopropyl alcohol. On adding the bromine water the hexane separated, forming a separate phase; moreover the free bromine was rapidly removed from both phases. A solution of bromine in hexane was tried, but was found to be extremely unpleasant to use, difficult to standardise and very volatile.

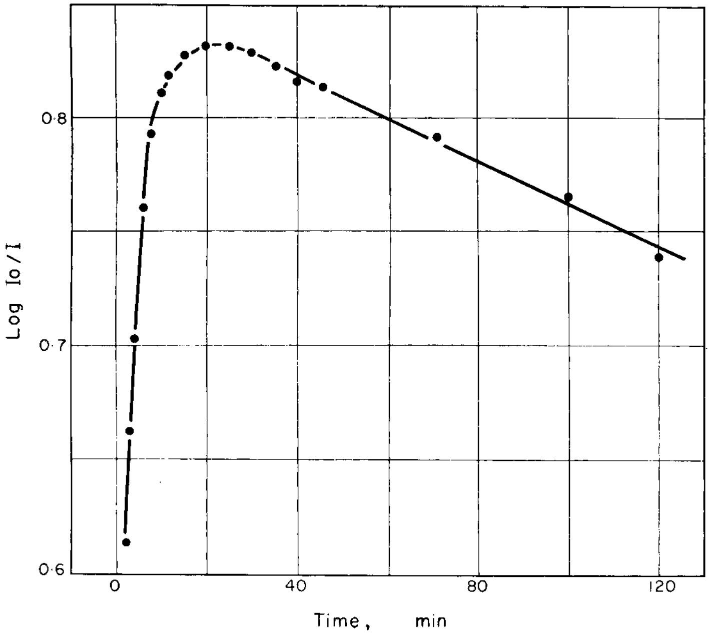

FIG. 3.—Variation of optical density with time:
● *n*-hexane-thiol
○ octadecane-thiol

On adding bromine water to the hexane solution, and shaking, most of the bromine is transferred to the organic layer, where the oxidation of the thiol to alkane sulphonyl bromide can then take place. This sulphonyl bromide can be extracted from the hexane phase into the aqueous phase by shaking with isopropyl alcohol. A measure of success was obtained using this procedure, which was therefore adopted as the arbitrary procedure from which variation of conditions was made.

Using the experience gained in the earlier work and using similar techniques it was possible to decide upon reaction times and reagent concentrations necessary to give maximum values of optical density. These are summarised below:

Bromine solution: The solution previously used for the alcoholic thiol solution, consisting of 5 volumes of saturated bromine water + 14 volumes of water, was found to give the maximum values of optical density. This solution was freshly prepared each day.

It was noted that inconsistent results were obtained with some dilute thiol solutions. This was attributed to some form of decomposition of the thiol before the addition of the bromine water. To prevent this, the order of addition of the thiol and bromine water was reversed, *i.e.*, the thiol was added to the bromine water. To ensure that no contaminating solution was left in the flasks used, they were left standing filled with dilute bromine water when not in use, and were washed out once with distilled water just before they were required.

Choice of solvent: A number of solvents were tried for the extraction of the alkane sulphonyl bromide from the hexane solution including acetone, industrial spirit, ethanol, dioxan and isopropyl alcohol. Of these the highest values of the optical densities of the coloured solutions were given when isopropyl alcohol was used.

It was also noted that if the extraction time was prolonged, the excess of bromine disappeared and low results were obtained. The optimum results were obtained when 2·25 ml of alcohol were allowed to react for 1 min.

Cyanide solution: Again a reaction time of 0·5 min was found to be suitable.

Aldridge's reagent: As before, a volume of 4 ml and a reaction time of 25 min were found to give maximum densities.

Temperature: Using a constant temperature water bath, reaction tests were carried out in the range 18–30°. At the higher temperature slight decreases in maximum optical density were recorded, but in the range 18–25° these values remained constant.

Procedure

Reagents: These were prepared as described earlier in this paper, with the exception of the diluted bromine water for which a dilution of 5 volumes of saturated solution + 14 volumes of water was employed.

Method: Transfer by pipette 1 ml of the diluted bromine water into a clean 10-ml measuring flask and add 2 ml of the thiol in hexane solution, having a maximum concentration of 0·5 μg of SH/ml. Shake the flask, preferably mechanically, for 5 min, add 2·25 ml of isopropyl alcohol and shake for a further 1 min.

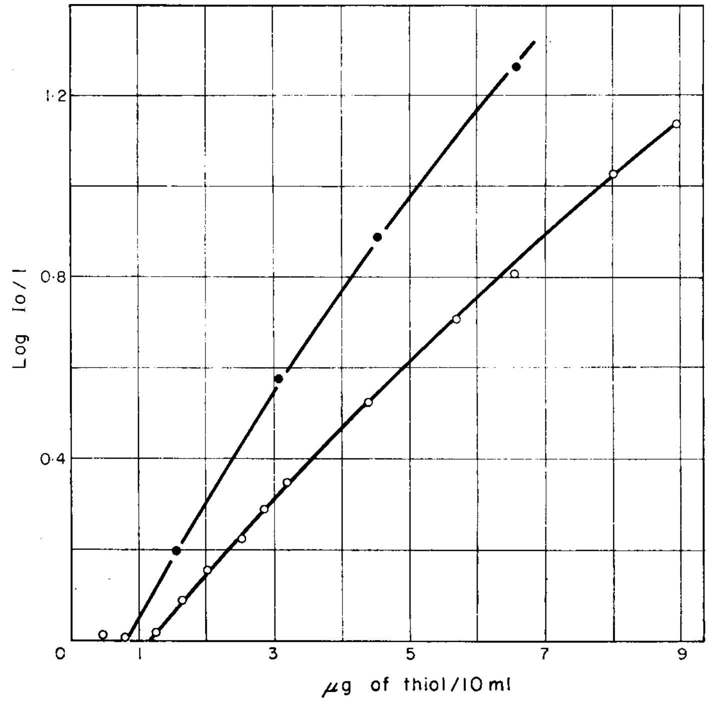

FIG. 4.—Calibration curves for *n*-hexane-thiol and octadecane-thiol: Unicam, 4-cm cells, 525 mμ.

Add 1 ml of phenol solution and shake by hand until all the colour of bromine has been discharged (a few sec only), add 1 ml of cyanide solution and shake, using the mechanical shaker, for 30 sec.

Add 4 ml of Aldridge's reagent and shake well by hand. After 15 min, remove the hexane layer with a pipette, dilute the solution to volume with distilled water, and mix well. Transfer the solution to a dry 4-cm spectrophotometer cell and allow to stand for about 7 min. The solution is usually slightly cloudy, but becomes clear on standing.

Measure the optical density using a spectrophotometer set at a wavelength of 525 mμ.

Calibration: In order to obtain calibration graphs, aliquots of diluted thiol solutions were examined by the procedure given above. These were prepared by dilution from concentrated thiol solutions standardised by titration with silver nitrate in an alcoholic ammoniacal medium with dithizone as indicator. This procedure is described by Kunkel *et al.*[4] Calibration curves for n-hexane-thiol and octadecane-thiol are shown in Fig. 4. These graphs indicate that the recovery of the thiol is not complete, possibly because of small quantities of alkane sulphonyl bromide remaining in the hexane layer. The quantities involved are: n-hexane-thiol, 0·92 μg (0·26 g of SH); octadecane-thiol, 1·36 μg (0·16 μg of SH).

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Zusammenfassung—Eine Methode zur Bestimmung von Thiolverbindungen in alkoholischen und Hexan-Lösungen im Konzentrationbereich 0·0005 bis 0·005 molar wird beschrieben. Die Methode folgt der von Saville beschriebenen, wonach die Thiolkomponente mittels Bromwasser zu einem Sulfonylbromid oxydiert wird. Auf Zusatz von Alkalicyanid formt dieses Bromcyan, welches sodann mit Aldridge's Reagens bestimmt wird.

Résumé—Les auteurs ont mis au point une méthode de dosage des thiols, dans des solutions d'alcool et d'hexane à des concentrations de 0,0005 M à 0,005 M. Cette méthode suit une technique décrite par Saville dans laquelle le thiol est oxydé en bromure de sulfonyle par l'eau de brome. Celui-ci, par addition de cyanure alcalin, forme du bromure de cyanogène qui est ensuite dosé en utilisant le réactif d'Aldridge.

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DIAMMONIUM-5,5′-INDIGO DISULPHONATE AS AN ANALYTICAL REAGENT

GRAVIMETRIC DETERMINATION OF THORIUM AND CERIUM^{III} AND THEIR SEPARATION FROM URANIUM^{VI}

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Summary—Diammonium-5,5′-indigo disulphonate forms insoluble complexes with many cations. Its use for the gravimetric determination of thorium and cerium^{III}, and their separation from uranium^{VI} has been investigated. Thorium and cerium^{III} are quantitatively precipitated within the pH range of 3·5 to 4·5 and 3·0 to 6·0 respectively, while uranium does not form any insoluble complex at this pH. The precipitate obtained in each case is ignited to the corresponding oxide and weighed.

INTRODUCTION

INDIGO carmine, the disodium salt of 5,5′-indigo disulphonic acid, has been used for the detection[1–13] and determination[1,14–22] of a large number of anions and cations. It has now been found that it also forms insoluble complexes with thallium^{I}, lead^{II}, calcium, barium, strontium, bismuth^{III}, yttrium, lanthanum, cerium^{III}, neodymium, samarium, dysprosium, zirconium^{IV}, thorium, molybdenum^{VI} and tungsten^{VI} from aqueous solutions of their salts.

The thorium and zirconium complexes are slightly soluble in water, and this leads to low results when they are washed with an excess of water. Because of the adsorption of sodium ions by the precipitate, an aqueous solution of the precipitant cannot be used as a wash liquid. This difficulty is avoided by using the diammonium salt of 5,5′-indigo disulphonic acid, the analytical behaviour of which is similar to that of indigo carmine.

For the determination of thorium, a large number of organic reagents have been reported in the literature,[23] but for its separation and determination in the presence of uranium there are few reagents which can be used successfully. Some of the important reagents which are suitable for this purpose are ferron,[24] *m*-nitrobenzoic acid,[25] anisic acid,[26] cinnamic acid,[27] *m*-cresoxyacetic acid,[28] sebacic acid[29] and 1-hydroxy-3-methoxyxanthone.[30]

The present authors find that diammonium 5,5′-indigo disulphonate, which is comparatively easy to prepare, can be successfully employed for the gravimetric determination of thorium at pH 3.5 to 4.5. Since the reagent does not form any insoluble complex with uranium even up to pH 9, it can be used for the separation of thorium from uranium.

There are only a few reagents which can be used for the determination of cerium alone or in the presence of other elements usually present in its minerals. The use of some of the common reagents, such as oxalic acid,[31] methyl oxalate[32] or potassium iodate,[33] is not convenient owing to the strict pH control which is necessary. Jefferson[34] used a number of organic bases but these do not offer any advantage over oxine.[35]

Though the results obtained with oxine are good, this reagent is not specific[36] and thus cannot effect the separation of cerium from uranium.

Diammonium 5,5′-indigo disulphonate has been found to precipitate cerium^{III} quantitatively in the pH range 3.0 to 6.0, and the results obtained are quite satisfactory. The determination of cerium when present alone or in the presence of uranium, up to about 10 times its amount, can readily be carried out.

EXPERIMENTAL

Preparation of the reagent

The method adopted for the preparation of diammonium 5,5′-indigo disulphonate was analogous to the one recommended[37] for the preparation of indigo carmine.

Five g of indigo (E. Merck, extra pure) with 55 ml of concentrated sulphuric acid (density 1·84) were heated in a water bath for about 1·5 hr, and then gradually poured into about 300 ml of cold water with constant stirring, and filtered hot. Solid ammonium carbonate was added to the filtrate till the ammonium salt of 5,5′-indigo disulphonic acid salted out. The mixture was then concentrated to about 250 ml and cooled in ice, and the diammonium 5,5′-indigo disulphonate was filtered off. The product, on recrystallisation from hot water, weighed 6·20 g, and did not melt up to 360°.

Reagents and equipment

All the metallic salts used were either of B.D.H. (AnalaR) or E. Merck (Pro Analysi) grade.

An aqueous solution (1 %) of the reagent was used as precipitant.

Hydrochloric acid, ammonia and glycine were used for adjustment of pH, which was measured with a Beckman pH Meter Model H2, using a suitable glass electrode.

Determination of thorium with diammonium 5,5′-indigo disulphonate

Two hundred and fifty ml of solution at pH 3·5–4·5, containing about 20 mg of thorium dioxide, were treated with 10 ml of a 10% aqueous solution of the reagent, with constant stirring. The mixture, on being kept at 80–90° for about 0·5 hr, produced a dark blue flocculent precipitate of the thorium complex, which, after cooling to room temperature, was filtered through Whatman No. 42 filter paper. The precipitate was washed with an aqueous solution (0·05%) of the reagent, dried, ignited and weighed as ThO_2.

Table I shows the results obtained with this reagent and those with oxine.

TABLE I.—DETERMINATION OF THORIUM

Wt. of ThO_2 present, *mg* (oxine method)	Wt. of ThO_2 found, *mg* (present reagent)
20·85	20·85
20·85	20·85
10·45	10·45
10·45	10·45
4·15	4·15
4·15	4·15

Effect of pH on the precipitation of the thorium complex

The effect of pH on the formation of the thorium complex with diammonium 5,5′-indigo disulphonate was studied by using ammonia and glycine as buffers for pH values higher than 3·5 and dilute hydrochloric acid for lower pH values. Though the reagent precipitates thorium in the range pH 1·0 to 7·5, the precipitation is quantitative only between pH 3·5 and 4·5.

Other common buffers containing acetate, phosphate and borate ions could not be used because of interference.

Determination of thorium in the presence of uranium^{VI}

Thorium in solutions containing varying quantities of uranium, was determined as described above. The results obtained are given in Table II.

TABLE II.—DETERMINATION OF THORIUM IN PRESENCE OF URANIUM

Wt. of ThO_2 taken, *mg*	Wt. of U_3O_8 present, *mg*	Wt. of ThO_2 found, *mg*
20·85	20·80	20·85
20·85	41·60	20·85
20·85	83·20	20·85
20·85	124·80	20·85
20·85	166·40	20·85
20·85	208·00	20·85

Determination of cerium^{III} *with diammonium 5,5′-indigo disulphonate*

To 200 ml of cerium^{III} solution (containing approximately 20 mg of CeO_2), at pH 5, about 10 ml of a 1 % aqueous solution of the reagent was added with constant stirring. The resultant mixture was kept at 90° for about 0·5 hr and then cooled to room temperature. The blue flocculent precipitate was filtered through Whatman No. 42 filter paper. The precipitate was washed with an aqueous solution (0·05 %) of the reagent, dried and ignited to the oxide. The results obtained are given in Table III.

TABLE III.—DETERMINATION OF CERIUM^{III}

Wt. of the CeO_2 present, *mg* (oxine method)	Wt. of the CeO_2 found, *mg* (present reagent)
19·75	19·75
19·75	19·75
9·90	9·90
9·90	9·90
5·00	5·00
5·00	5·00

Effect of pH on the formation of the cerium^{III} *precipitate*

The effect of pH (range 1·0 to 8·5) on the formation of the cerium^{III} complex was investigated using ammonia and glycine as buffers for pH values higher than 5·0 and hydrochloric acid for lower values. Though cerium^{III} is precipitated between pH 1·5 and 8·0, the precipitation is only quantitative between pH 3·0 and 6·0.

TABLE IV.—DETERMINATION OF CERIUM^{III} IN THE PRESENCE OF URANIUM^{VI}

Wt. of CeO_2 taken, *mg*	Wt. of U_3O_8 added, *mg*	Wt. of CeO_2 found, *mg*
19·75	20·80	19·75
19·75	52·00	19·70
19·75	104·00	19·75
19·75	156·00	19·75
19·75	208·00	19·75

Determination of cerium^{III} in the presence of uranium^{VI}

As the reagent does not form an insoluble complex with uranium^{VI}, even at pH 9·0, the determination of cerium^{III} in the presence of uranium^{VI} can readily be carried out.

Solutions of cerium^{III} containing varying amounts of uranium^{VI}, at pH 5·0, were taken and the determination of its cerium content was carried out using the reagent as described above. The results obtained are given in Table IV.

Investigations on the determination of zirconium, and on its separation from other elements with the help of this reagent are in progress.

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Zusammenfassung—Diammonium-5-5′-indigodisulfonat bildet unlösliche Komplexe mit zahlreichen Kationen. Seine Anwendung zur gravimetrischen Bestimmung von Thorium und Cer(III) sowie zur Trennung der beiden von Uran(VI) wurde untersucht. Thorium und Cer(III) werden quantitativ gefällt im pH-Bereich 3·5–4·5 bzw. 3·0–6·0, während Uran in diesem Bereich keinen unlöslichen Komplex bildet. Die erhaltenen Niederschläge werde zu den entsprechenden Oxyden verglüht und gewogen.

Résumé—Le disulfonate de diammonium-5,5′-indigo forme des complexes insolubles avec de nombreux cations. Son utilisation pour le dosage gravimétrique du thorium et du cérium(III) et la séparation de ces derniers de l'uranium(VI) a été étudiée. Le thorium et le cérium(III) sont précipités quantitativement dans les domaines de pH: 3,5–4,5 et 3,0–6,0 respectivement, alors que l'uranium ne forme pas de complexes insolubles à ces valeurs de pH. Le précipité obtenu dans chaque cas est calciné pour former l'oxyde correspondant et pesé.

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ÜBER DIE ANWENDUNG VON CYSTEIN ALS MASKIERUNGSREAGENS BEI KOMPLEXOMETRISCHEN TITRATIONEN

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Zusammenfassung—Cystein bildet in schwach saurer Lösung mit einer Reihe von Kationen farblose, lösliche Komplexe. Die Komplexe mit Quecksilber und Kupfer sind stabiler als die entsprechenden Komplexe der Äthylendiamintetraessigsäure, was zur Maskierung der genannten Metalle bei komplexometrischen Titrationen ausgenützt wurde. Beschrieben ist die Bestimmung von Zn^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Al^{3+} und Fe^{3+} in Gegenwart grösserer Mengen Quecksilber oder Kupfer bzw. die Bestimmung dieser zwei Metalle und der anderen angeführten Kationen nebeneinander.

CYSTEIN bildet mit einer Reihe von Kationen sehr stabile Komplexe. Diese Eigenschaft des Cysteins wurde schon früher zu analytischen Zwecken ausgenützt. Beschrieben wurde z.B. schon eine Methode zur potentiometrischen Cysteinbestimmung mit Quecksilbernitratlösung,[1] sowie die volumetrische Bestimmung von Quecksilber und Nickel mit einer Cysteinlösung in alkalischem Medium.[2] Uns interessierte, ob sich die Bildung der Cystein-Metall-Komplexe nicht auch zur Maskierung mancher Kationen bei komplexometrischen Titrationen ausnützen liesse. Dabei zeigte sich, dass einige Metalle mit Cystein wirklich bedeutend festere Komplexe bilden als mit Äthylendiamintetraessigsäure, so dass diese Aminosäure bei einer Reihe von Bestimmungen mit Erfolg als Maskierungsreagens verwendet werden kann. Stabile Metallkomplexe bildet Cystein sowohl in alkalischen als auch in sauren Lösungen. In alkalischer Lösung sind die Verhältnisse jedoch sehr kompliziert, sodass hier noch ein weiteres Studium erforderlich ist.

In dieser Arbeit beschreiben wir vorläufig die Anwendung von Cystein als Maskierungsreagens bei Titrationen in saurer Lösung. Die im weiteren angeführten Ergebnisse zeigen, dass mit Cystein die Reihe der bisher bekannten Maskierungsreagenzien um einen neuen, interessanten und vorteilhaften Stoff bereichert wird.

REAKTIONEN DES CYSTEINS

In schwach saurer Lösung

Bei pH 5,5 reagiert Cystein mit Quecksilber unter Bildung eines weissen Niederschlages, der sich bei weiterer Zugabe von Cystein zu einer farblosen Lösung auflöst. Der sich bildende Komplex ist fester als der Quecksilberkomplex der Äthylendiamintetraessigsäure.

Thallium gibt mit Cystein eine braune Färbung. Durch weitere Zugabe von Cystein entsteht ebenfalls eine farblose Lösung. Hierbei handelt es sich jedoch um die Reduktion von Tl^{3+} zu Tl^{1+}. Da Tl^{1+} bei diesem pH nicht komplexometrisch bestimmt werden kann, lässt sich auch diese Reaktion zur Selektivitätserhöhung mancher Titrationen ausnützen.

Kupfer liefert mit Cystein erst eine schmutzigviolette Färbung, dann einen schmutzigen Niederschlag, der durch einen Überschuss von Cystein ebenfalls in eine farblose Lösung übergeführt werden kann. Obwohl auch dieser Komplex fester ist als der Kupferkomplex der Äthylendiamintetraessigsäure, ist Cystein zur Maskierung von Kupfer nur beschränkt anwendbar. In Gegenwart anderer Kationen z.B. Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} entsteht nämlich nicht der farblose, lösliche Kupferkomplex, sondern es bilden sich verschiedenartig gefärbte Niederschläge. Diese Niederschläge wurden zwar nicht näher untersucht, höchstwahrscheinlich handelt es sich aber um Produkte, bei denen an Cystein ausser Kupfer auch noch das zweite Metall gebunden ist. Die Niederschläge sind in Wasser teilweise, in Komplexon vollständig löslich. Mit Komplexon können sie sogar sehr vorsichtig titriert werden; praktischen Wert hat so eine Titration allerdings nicht. Aus dem Gesagten geht hervor, dass Cystein zur Maskierung von Kupfer nur bei Rücktitrationen verwendet werden kann, wo der Komplexonüberschuss die Ausfällung der erwähnten Mischkomplexe verhindert.

Mit Cadmium gibt Cystein einen weissen Niederschlag, der durch weitere Zugabe von Cystein nicht vollkommen in Lösung gebracht werden kann. Aus dem Äthylendiamintetraessigsäurekomplex wird Cadmium durch Cystein nur unvollständig verdrängt. Daraus geht hervor, dass die Festigkeit des Cystein-Cadmium-Komplexes nicht von der Grössenordnung ist, die zu einer einwandfreien Maskierung notwendig ist.

Mit Wismut bildet Cystein einen löslichen, farblosen Komplex, der etwas fester ist als der Wismutkomplex der Äthylendiamintetraessigsäure. Der Unterschied in der Festigkeit beider Komplexe ist jedoch nicht gross genug um die einwandfreie Maskierung von Wismut zu garantieren.

Zink, Blei, Kobalt und Nickel bilden mit Cystein farblose, lösliche Komplexe. Aluminium und Eisen reagieren bei pH 2–3 mit Cystein ebenfalls unter Bildung löslicher Komplexe. Der Aluminiumkomplex ist farblos, der Eisenkomplex blau, seine Farbe wird jedoch mit der Zeit immer schwächer. Wird der pH-Wert der Lösung auf 5,5 eingestellt, so bleiben beide Kationen weiter als Komplexe in Lösung. Eisen bildet bei diesem pH-Wert ebenfalls einen farblosen Komplex. Die Komplexe aller dieser Kationen sind bedeutend schwächer als die entsprechenden Komplexe der Äthylendiamintetraessigsäure, so dass es möglich ist sie in Gegenwart von Cystein direkt oder indirekt mit Komplexon zu titrieren.

Die Reaktionen von namentlich nicht angeführten Kationen wurden nicht untersucht.

Auf Grund der beschriebenen Reaktionen kann gesagt werden, dass sich Cystein bei pH 5,5 zum Maskieren von Quecksilber in Gegenwart von Zink, Blei, Aluminium, Kobalt, Nickel und Eisen eignet. Störend wirken Cadmium und Wismut. Kupfer stört bei direkten Titrationen ebenfalls, bei Rücktitrationen kann es jedoch durch Cystein maskiert werden.

In alkalischer Lösung

Der Vollständigkeit wegen seien noch kurz die Reaktionen einiger Kationen mit Cystein in alkalischer Lösung angeführt.

Bei pH 11 bildet Cystein sehr feste farblose und lösliche Komplexe mit Quecksilber, Zink, Cadmium und Wismut. Alle diese Metalle können mit Cystein gegen Komplexon maskiert werden.

Blei bildet ebenfalls einen löslichen farblosen Komplex, der jedoch schwächer ist als der Bleikomplex der Äthylendiamintetraessigsäure. Cystein maskiert Blei nur gegen die Indikatoren Eriochromschwarz T oder Methylthymolblau.

Calcium, Barium, Magnesium, Aluminium und Mangan bilden mit Cystein entweder gar keine oder nur sehr schwache, farblose, lösliche Komplexe. Diese Metalle können in Gegenwart von Cystein direkt oder indirekt mit Komplexon titriert werden.

Kupfer bildet mit Cystein einen löslichen, intensiv braun gefärbten Komplex, der fester ist als der Kupferkomplex der Äthylendiamintetraessigsäure. Wegen der intensiven Farbe kann die Bildung dieses Komplexes jedoch nicht zur Maskierung von Kupfer ausgenützt werden. Die bekannte Blockierung von Eriochromschwarz T durch Kupfer lässt sich durch Zugabe von Cystein nicht verhindern.

Kobalt, Nickel und Eisen bilden mit Cystein Komplexe, deren Farbe und Festigkeit von der Reihenfolge abhängen, in der der Lösung Cystein, Puffer und eventuell Komplexon zugesetzt werden.

In alkalischen Lösungen treten einige Erscheinungen auf, die sich, ähnlich wie bei Kupfer in saurer Lösung, am besten durch Bildung von Mischkomplexen erklären lassen. So lassen sich z.B. Cadmium und Zink in Gegenwart von Magnesium oder Mangan nicht mit Cystein maskieren, obwohl beide Metalle für sich allein so feste Cysteinkomplexe bilden, dass die Maskierung möglich ist. Diese Erscheinungen erschweren selbstverständlich die praktische Anwendung von Cystein zum Maskieren in alkalischen Lösungen; sie sind Gegenstand weiterer Untersuchungen.

EXPERIMENTELLER TEIL

Reagenzien

Die 0,05 M-Komplexon-(III)-Lösung wurde auf bekannte Weise hergestellt.

Die 0,05 M Lösungen von Hg^{2+}, Tl^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Bi^{3+}, Ni^{2+}, Co^{2+}, Fe^{3+} und Al^{3+} wurden aus den entsprechenden Nitraten bzw. Sulfaten (Reinheit p.a.) hergestellt. Alle Lösungen waren schwach mit Salpetersäure angesäuert. Die Titer aller Lösungen wurden komplexometrisch kontroliert.

Das verwendete l-Cystein war ein Erzeugniss der Fy. Lachema, Brno. Es wurde den Lösungen in fester Form zugesetzt.

Xylenolorange kam als 0,5% ige wässrige Lösung zur Anwendung.

Als Pufferlösung wurde eine 20%ige wässrige Urotropinlösung verwendet.

Analysenbeispiele

1. *Die Bestimmung von* Zn^{2+} (Pb^{2+}) *in Gegenwart von* Hg^{2+}: Die schwach saure Lösung wird mit 10 ml einer 20%igen Urotropinlösung versetzt. Weiter werden Cystein und einige Tropfen Xylenolorange zugegeben. Nun wird mit 0,05 M Komplexonlösung bis zum Auftreten der gelben Farbe titriert. Der Verbrauch an Komplexonlösung entspricht dem Zink- oder Bleigehalt.

2. *Die Bestimmung von* Zn^{2+} (Pb^{2+}) *und* Hg^{2+} *nebeneinander:* Zuerst wird in mit Urotropin gepufferter Lösung die Summe der Kationen durch direkte Titration gegen Xylenolorange bestimmt. Dann wird der Lösung Cystein zugesetzt und das freigewordene Komplexon, dass dem Quecksilber gehalt entspricht, wird mit 0,05 M Bleinitratlösung titriert. Der Farbumschlag verläuft hierbei von reingelb nach blauviolett.

3. *Die Bestimmung von* Co^{2+} (Ni^{2+}, Al^{3+}, Fe^{3+}) *in Gegenwart von* Hg^{2+} (Cu^{2+}): Die saure Lösung (pH 2–3) wird mit einem Überschuss der 0,05 M Komplexon(III)-Masslösung versetzt. Dann wird Cystein zugeben. Der pH-Wert der Lösung wird nun mit Urotropin auf 5,5 eingestellt und nach Zugabe einiger Tropfen Xylenolorange wird mit 0,05 M Bleinitratlösung zurücktitriert. Die Menge des nicht zurücktitrierbaren Komplexons entspricht dem Kobalt-, Nickel-, Aluminium-oder Eisengehalt Sollen die angeführten Kationen neben Kupfer bestimmt werden, so empfiehlt es sich, die Titration in der Wärme durchzuführen. Die Verdrängung des Kupfers aus dem Äthylendiamintetraessigsäurekomplex durch Cystein verläuft in der Kälte nämlich etwas zu langsam. Bei Titrationen in der Wärme ist es der besseren pH-Einhaltung wegen vorteilhafter anstelle des normalen Urotropinpuffers

Urotropin- oder Acetatpuffer mit Salpetersäurezusatz zu verwenden (z.B. eine Lösung von 140 g Urotropin und 120 ml 1 N HNO_3 oder 200 g Natriumacetat und 150 ml 1 N HNO_3 in 1 Liter Wasser). Auf die beschriebene Weise kann neben Kupfer auch Zink oder Blei bestimmt werden.

4. *Die Bestimmung von* Co^{2+} (Ni^{2+}, Al^{3+}, Fe^{3+}) *und* Hg^{2+} (Cu^{2+}) *nebeneinander:* Die saure Lösung (pH 2–3) wird mit einem Überschuss der 0,05 M Komplexon(III)-Masslösung versetzt. Der pH-Wert der Lösung wird nun mit Urotropin auf 5,5 gebracht und nach Zugabe einiger Tropfen Xylenolorange wird der Überschuss des Komplexons mit 0,05 M Bleinitratlösung retitriert. Auf diese Weise wird die Summe der Kationen bestimmt. Nun wird Cystein zugegeben und das freigewordene Komplexon, das dem Quecksilber-, oder Kupfergehalt entspricht wird mit 0,05 M Bleinitratlösung weitertitriert. Aus Gründen, die schon im vorigen Beispiel angeführt wurden, ist es auch hier bei Kupferbestimmungen empfehlenswert in der Wärme zu arbeiten und Pufferlösungen mit Salpetersäurezusatz zu verwenden. Auf gleiche Weise können auch Zink oder Blei und Kupfer nebeneinander bestimmt werden.

DISKUSSION

Cystein eignet sich bei komplexometrischen Titrationen in schwach sauren Lösungen zum Maskieren von Quecksilber. Cadmium und Wismut stören. Kupfer stört bei direkten Titrationen ebenfalls, bei Rücktitrationen kann es jedoch mit Cystein maskiert werden. In Tabelle 1 sind die Ergebnisse einiger Analysen zusammengestellt, die unter Zuhilfenahme von Cystein als Maskierungsreagens durchgeführt wurden. Aus der Tabelle geht hervor, dass bei diesen Analysen die gleiche Genauigkeit ereicht wird, wie bei anderen komplexometrischen Titrationen.

TABELLE I.—KOMPLEXOMETRISCHE BESTIMMUNG EINIGER KATIONEN IN SCHWACH SAURER LÖSUNG BEI ANWENDUNG VON CYSTEIN ALS MASKIERUNGSREAGENS.

Analysen-vorschrift	gegeben, *mg*	gefunden, *mg*
1	Pb 103,6 Hg 200,6	Pb 103,8
2	Zn 6,5 Hg 100,3	Zn 6,5 Hg 100,5
3	Co 11,8 Hg 40,1	Co 11,7
	Fe 14,0 Hg 40,1	Fe 13,9
	Ni 15,0 Cu 6,3	Ni 15,2
	Zn 19,5 Cu 12,6	Zn 19,5
4	Ni 15,0 Hg 80,2	Ni 14,9 Hg 80,3
	Co 14,7 Cu 12,6	Co 14,7 Cu 12,7
	Fe 8,4 Cu 15,9	Fe 8,4 Cu 15,8
	Pb 20,8 Cu 31,8	Pb 20,6 Cu 31,9

Vergleichen wir Cystein mit Thiosemikarbazid, das von Körbl und Přibil[3] zur Maskierung von Quecksilber in schwach sauren Lösungen empfohlen wurde, dann sehen wir, dass sich beide Stoffe gut ergänzen. In Gegenwart von Eisen ist es z.B. nicht gut möglich Quecksilber mit Thiosemikarbazid zu maskieren; Cystein dagegen kann sehr wohl angewendet werden. Cadmium und Wismut dagegen machen das Arbeiten mit Cystein unmöglich, während sie die Anwendung von Thiosemikarbazid nicht stören.

Kupfer kann mit Cystein zwar nur bei Rücktitrationen maskiert werden, es sind aber hier einige Bestimmungen möglich (z.B. Cu und Fe, Co oder Ni nebeneinander), die früher nur auf kompliziertere Weise[4] durchgeführt werden konnten.

Erfolgversprechend ist auch die kombinierte Maskierung von Kationen mit Cystein und anderen Maskierungsreagenzien. Als Beispiel seien o-Phenanthrolin[5] oder α,α'-Dipyridyl[6] genannt, die in schwach saurer Lösung ausser Blei und Aluminium fast alle in Frage kommenden Kationen maskieren.

Noch nicht zufriedenstellend gelöst ist die Anwendung von Cystein als Maskierungsreagenz bei komplexometrischen Titrationen in alkalischer Lösung. Diese Möglichkeit wird jedoch von uns weiter verfolgt.

Summary—In weakly acid solutions cysteine forms colourless soluble complexes with a series of cations. The complexes with mercury and copper are more stable than the corresponding complexes with ethylenediaminetetra-acetic acid, so that they can be used for masking purposes in complexometric titrations of these ions. The determination of Zn^{2+}, Pb^{2+}, Ni^{2+}, Al^{3+} and Fe^{3+}, in the presence of larger amounts of mercury or copper, and of these last two and the series of ions listed in the presence of one another.

Résumé—En solution faiblement acide, la cystéine forme des complexes incolores solubles avec une série de cations. Les complexes avec le mercure et le cuivre sont plus stables que les complexes correspondants avec l'acide éthylènediaminetétracétique, de sorte qu'ils peuvent être utilisés comme agents complexants dans les titrages complexométriques de ces ions. On peut doser Zn^{2+}, Pb^{2+}, Ni^{2+}, Al^{3+} et Fe^{3+} en présence de grandes quantités de mercure ou cuivre, ainsi que ces deux derniers et la série des ions énumérés en présence de chaque autre.

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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM WITH 3,3'-DIAMINOBENZIDINE

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Summary—A simple, rapid and highly selective method for determining small amounts of vanadium has been developed based on the oxidation of diaminobenzidine with vanadate ion. The reaction is best carried out in a phosphoric acid medium. The molar ratio of the reaction was found to be 1:1. The sensitivity and molar absorptivity of the method were found to be 0·016 μg of vanadium per cm^2 for log $I_0/I = 0{\cdot}001$, and 3,310, respectively.

INTRODUCTION

This paper describes a new spectrophotometric method for the determination of small amounts of vanadium, based on an oxidation colour reaction of 3,3'-diaminobenzidine (DAB) with vanadate ion in an acidic medium. The rate of oxidation is dependent upon the acid concentration and the kind and quantity of acid present. The acid concentration is not critical, however, when phosphoric or perchloric acid is employed. Because versatile and sensitive analytical methods for determining small amounts of vanadium are not abundant, the use of DAB as an analytical reagent for vanadium was investigated.

DAB has been proved to be an excellent reagent for selenium.[1,2] Hoste[2] first reported a qualitative test for vanadium using DAB, and later Cheng[1] pointed out that vanadate^{V} oxidised DAB in the presence of EDTA (ethylenediaminetetra-acetic acid) in a weakly acidic medium; so far, however, no quantitative procedure for vanadium which uses DAB has appeared in the literature. Because of its high selectivity and fair sensitivity, an attempt to develop a quantitative method for vanadium, utilising the colour reaction, was undertaken.

APPARATUS

Beckman Model DU spectrophotometer equipped with 1-cm cells.

REAGENTS

Standard vanadium solution: Prepared from ammonium metavanadate, 50 μg per ml.

Phosphoric acid: 85% (density = 1·80).

3,3'-Diaminobenzidine tetrachloride (DAB) solution: Freshly prepared before use, 1×10^{-2} *M*. The pure reagent is snow white in colour. Some of the material on the market showed a reddish or purplish colour caused by air oxidation. It should be kept in a refrigerator under an inert atmosphere. The properly stored material is indefinitely stable.

Other reagents used were analytical reagents.

Preparation of calibration curve

To a solution containing 25–250 μg of vanadium in a 25-ml calibrated flask add 1 ml of 85% phosphoric acid and dilute to approximately 20 ml with water. Cool, add 1 ml of 10^{-2} *M* DAB solution (freshly prepared), make to the mark with water, and mix. Measure the absorbance at 470 mμ, using a reagent blank, after standing for 15 min.

DEVELOPMENT OF METHOD

Absorption spectra

The oxidation product of DAB by vanadate is reddish-brown and has three absorption maxima at 340, 380, and 470 mμ. The DAB solution is slowly oxidised by air and shows similar maxima (Fig. 1). The maximum of 470 mμ was chosen for all measurements in this study.

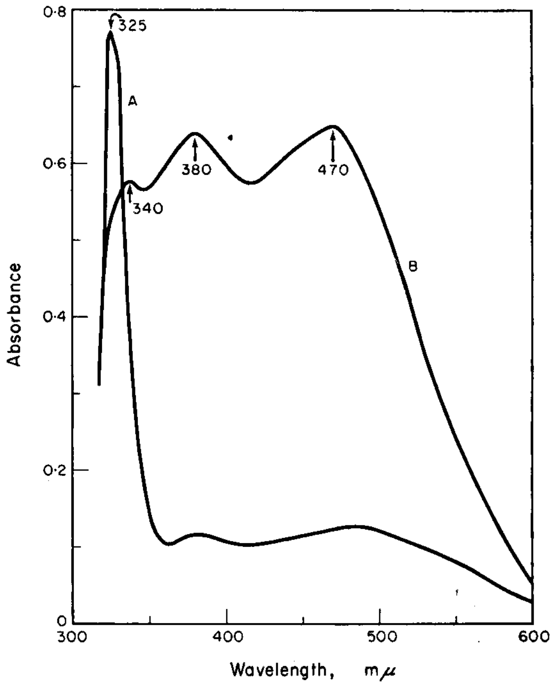

FIG. 1.—Absorption spectra.
A—DAB ($10^{3}M$) oxidised by air for 2 days in 0·3M H_3PO_4.
B—25 μg of vanadium + 0·01 mmole of DAB + 15 mmoles of H_3PO_4.
Total volume 25 ml: 1-cm cell.

Effect of acidity

The colour reaction is best carried out in a solution containing 0.02–0.2 ml of 85% phosphoric acid per ml volume. More phosphoric acid may be added, but if this is done a calibration curve using the same amount of phosphoric acid should be prepared. The reaction may also be carried out in the presence of EDTA, which is used as a masking agent, at pH 2–3, but the colour develops rather slowly in a less acidic medium. The curves in Fig. 2 indicate that both phosphoric acid and perchloric acid can be used over a wide range of acid concentrations, without significant effect, and that only limited amounts of other acids should be present because they may decrease the colour intensity. Their inhibiting effect may be attributed to the change in the oxidation potential of vanadate in different acid media. For a 25-ml volume, 10 ml of glacial acetic acid completely masked the colour development. Small amounts of tartaric or citric acid also masked the colour reaction, because of reduction of vanadate, or complex formation. The use of phosphoric acid is preferred, because it gives maximum colour development independent of its concentration, and also because it complexes iron^{III} giving a colourless solution, and preventing the iron^{III} from oxidising DAB.

Effect of amount of DAB

The curves in Fig. 3 show that 10 μmoles of DAB are sufficient for less than 300 μg of vanadium. Actually the excess amount of DAB has no effect on the blank because the freshly prepared solution is colourless. These curves also indicate a 1: 1 reaction between DAB and vanadate.

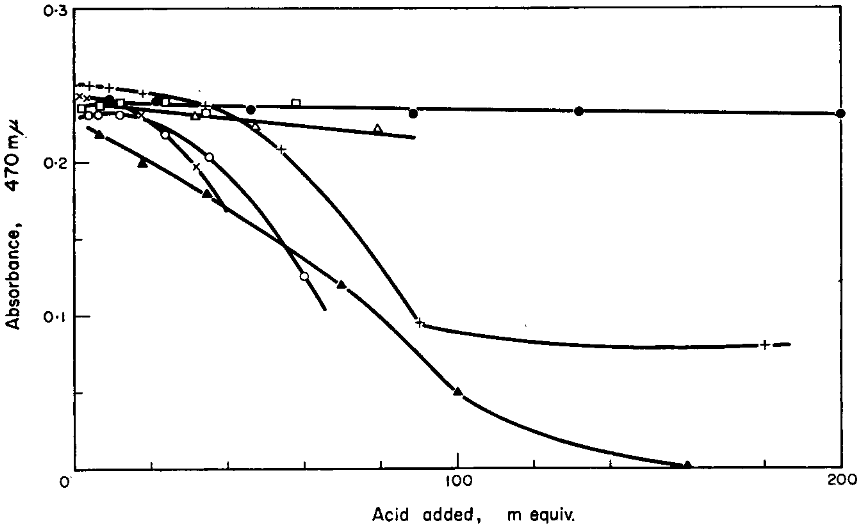

FIG. 2.—Effect of acid on oxidation of DAB with vanadate.
□—$HClO_4$: ●—H_3PO_4: △—HNO_3:
○—HCl: +—H_2SO_4: ▲—HOAc: ×—HBF_4.

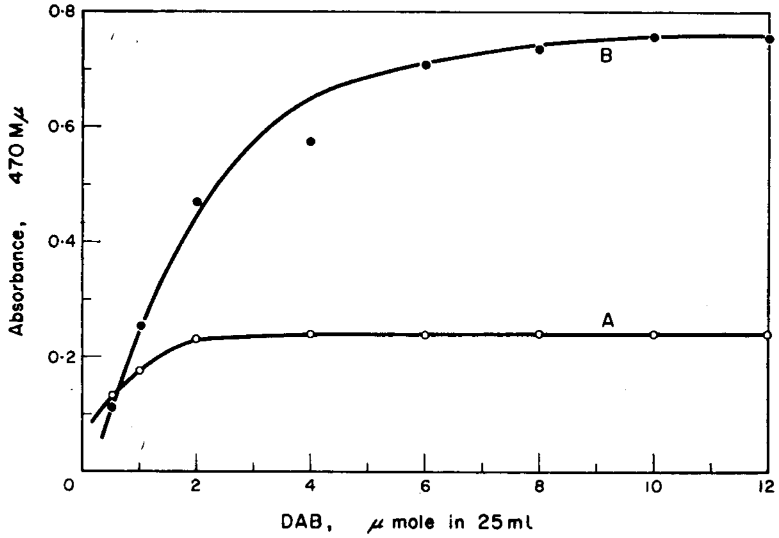

FIG. 3.—Effect of amount of DAB.
A—2μ moles of vanadium.
B—6μ moles of vanadium.

Beer's law

Beer's law was followed for 1–25 μg of vanadium per ml in a phosphoric acid medium, as shown in Fig. 4. At pH 2.5 the colour development was slow, especially for low concentrations of vanadium, because the oxidation potential of vanadate ion to vanadyl ion decreases with decrease in acidity. Furthermore, the rate of oxidation is probably influenced by the catalytic action of the intermediate products as evidenced by the much slower colour development of lower concentrations of vanadium. Maximum colour development may be obtained when the solutions are allowed to to stand for 2 hr or longer.

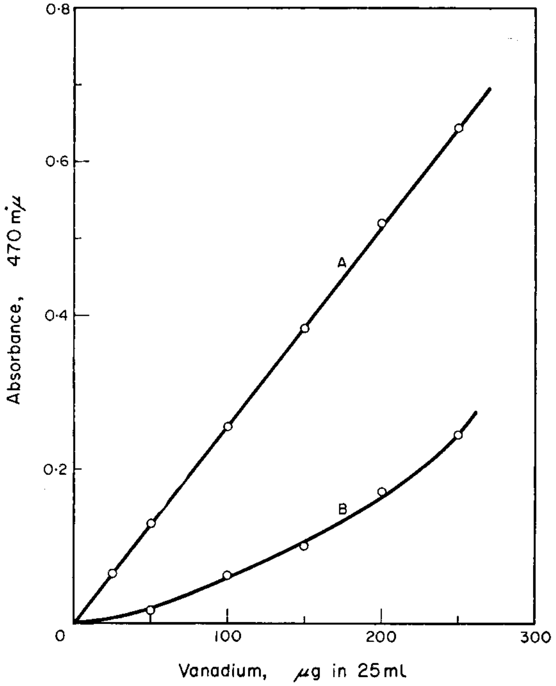

Fig. 4.—Calibration curve.
A—1 ml of 85% phosphoric acid added: standing for 15 min.
B—0·025 mmole of EDTA added, pH 2·5: standing for 30 min.

Stability

The colour reaction developed rapidly in a phosphoric acid medium. It is recommended that the absorbance be measured after standing for 15 min. After standing for 1 hr the absorbance shows no significant change. Any unnecessary delay in measurement of absorbance should, however, be avoided, because air slowly oxidises DAB. Therefore a reagent blank should always be made.

Sensitivity

The DAB reaction for vanadium is fairly sensitive. The sensitivity is 0.016 μg of vanadium per cm^2 for $\log I_0/I = 0.001$. The molar absorptivity is 3,310. The DAB method is more sensitive than the classic hydrogen peroxide method.

INTERFERENCES

Cations

DAB, like other amines, is easily oxidised; hence any strong oxidising reagent interferes. For example, chromium^{VI} interferes but chromium^{III} does not. Highly coloured solutions interfere, however; with weakly coloured solutions the interference may be eliminated by correction with a sample blank. According to Hoste, in the absence of oxidising agents the DAB reaction is specific for vanadium^{V}. The interference of iron^{III} can be eliminated by phosphoric acid or by pyrophosphate. Large amounts (say, 0.1 g) showed some interfering effect, however, even in the presence of 5 ml of 85% phosphoric acid. It seemed that there was sufficient iron^{III} ion dissociated from the ferric-phosphate complex to oxidise DAB. When a sample is dissolved in hydrochloric acid or a mixture of hydrochloric acid and nitric acid, vanadium can be oxidised to vanadate, but cerium, manganese, or chromium cannot be oxidised to the highest oxidation state by nitric acid. Under ordinary conditions, the DAB reaction for vanadium seems to be highly selective. The results shown in Table I were obtained when vanadium was determined in the presence of the metals which are often present with vanadium or which interfere in the methods commonly used for vanadium. These results are satisfactory. Amounts of iron^{III} as large as 10 mg did not interfere. For unusual amounts of iron, it may be necessary to separate by electrolysis,[3] solvent extraction, or ion exchange[4] before attempting the vanadium determination. Traces of selenium produced no significant effect; large amounts interfere and may be separated by solvent extraction.[1] The oxidation product of DAB is not extracted by benzene or toluene.

TABLE I.—DETERMINATION OF VANADIUM IN PRESENCE OF FOREIGN METALS

(100 μg of vanadium taken in 25 ml)

Metal present*	Vanadium found, μg
Iron^{III}	102·2
Chromium^{III}	97·4
Titanium^{IV}	98·5
Niobium^{V}	100·0
Tantalum^{V}	100·5
Tin^{IV}	97·8
Molybdenum^{VI}	99·2
Zirconium^{IV}	100·2
Copper^{II}	100·5
Tungsten^{VI}	100·2
Manganese^{II}	100·0

* The amount present was 1×10^{-2} mmole, except for iron when it was 10 mg.

Anions

As shown in Fig. 2, the solution should contain mainly phosphate or perchlorate anions; small amounts of other anions are tolerable, but large amounts of the other anions shown in Fig. 2 should be removed. This is easily done by evaporating the solution to dryness or nearly so, then evaporating again with phosphoric acid. Addition of organic acids should be avoided, because they may complex vanadium, or may reduce it to its lower oxidation state, which does not oxidise DAB. Both tartrate and citrate masked the vanadate reaction with DAB; the former reduced vanadate ion, and formed a strongly coloured yellow complex. Fluoride showed no effect; therefore, for special occasions, it may be advantageous to add fluoride as a masking agent. For instance, tantalum is more easily hydrolysed than niobium; it is difficult to keep tantalum in solution in phosphoric acid medium. Addition of fluoride helps to do this. Hydrogen peroxide did not oxidise DAB in a phosphoric acid medium, but it did inhibit colour development by forming a stable peroxy complex with vanadium.

COMPARISON OF DAB WITH RELATED COMPOUNDS

The colour development of vanadate with 3,3'-diaminobenzidine may be made in a wide range of concentrations of phosphoric or perchloric acid. Nitrate does not oxidise the reagent. The reproducibility is excellent. The reagent solution containing phosphoric acid remains colourless even when allowed to stand for more than 10 hr. Sulphate and tungstate form no precipitates with the reagent in a strongly acidic medium.

Diphenylamine and its sulphuric acid derivative are oxidised by nitrate.[5] The reproducibility is poor.[6] Diphenylbenzidine is also oxidised by nitrate, and colour development with vanadate requires a high concentration of phosphoric acid.[7] The interference arising from precipitation by sulphate and tungstate is serious. 3,3'-Dimethylnaphthidine often gives a colour in the blank. The slow colour development may be improved by using a mixture of phosphoric acid and perchloric acid, but a high concentration of acid is necessary for maximum colour development.[8] Poor reproducibility in the determination of vanadium in steel has been reported.[9]

Zusammenfassung—Eine einfache und hochselektive Schnellmethode zur Bestimmung kleiner Vanadinmengen wurde entwickelt. Die Methode beruht auf der Oxydation von Diaminobenzidin durch Vanadationen. Die Reaktion verläuft am besten in phosphorsaurem Medium. Es wurde gefunden, dass das Molverhältnis der Reaktanten 1:1 ist. Die Empfindlichkeit der Reaktion ist 0·016 μg V per cm^2 für 0·001 Absorption. Der molare Extinktionkoeffizient beträgt 3310.

Résumé—L'auteur a mis au point une méthode simple, rapide et très sélective de dosage de faibles quantités de vanadium. Cette méthode est basée sur l'oxydation de la diaminobenzidine par l'ion vanadate. La réaction est réalisée dans les meilleurs conditions en milieu acide phosphorique. Le rapport molaire de la réaction est 1/1. La sensibilité et le coefficient d'extinction molaire sont respectivement 0,016 μg de vanadium par cm^2 pour log $I_0/I = 0{,}001$, et 3310.

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GRAVIMETRIC DETERMINATION OF TUNGSTEN BY HOMOGENEOUS PRECIPITATION*

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Summary—A homogeneous precipitation method has been developed for the gravimetric determination of tungsten, by thermal decomposition of soluble peroxytungstate from a nitric acid-hydrogen peroxide solution. It appears that in all cases, especially for small concentrations, the tungsten recovery is superior to the classical techniques using cinchonine or β-naphthoquinoline. Furthermore, co-precipitation of molybdenum and vanadium are reduced to a considerable extent. The study of the co-precipitation process shows that the distribution coefficients follow a linear pattern for both contaminants. The method has been tested with good results on a number of standard tungsten alloy steels, corrections for incomplete precipitation and co-precipitation being applied on the basis of the experimentally found values.

THE gravimetric determination of tungsten usually involves the use of organic reagents such as cinchonine or β-naphthoquinoline to ensure a quantitative precipitate of tungstic acid.

Leliaert, Hoste and Eeckhaut[1] recently proposed a homogeneous precipitation method for tungstic acid, by thermal decomposition of soluble peroxytungstic acid from a hydrogen peroxide medium. A quantitative precipitate was not required in this case, as an isotope dilution technique was used. From preliminary experiments[2] it appeared, however, that this method is capable of giving quantitative results, co-precipitation of molybdenum and vanadium being considerably reduced.

Radioactive tracer techniques were used to develop the proposed method.

Radio-isotopes

Tungsten: ^{187}W, β, γ-emitter, half life 24 hr, produced by irradiation of WO_3 in the BR-1 reactor.

Molybdenum: ^{99}Mo, β, γ-emitter, half life 67 hr, produced by irradiation of molybdic oxide in the BR-1 reactor.

Vanadium: ^{48}V, β, γ-emitter, half life 16 d, produced by 22 MeV deuteron bombardment of titanium. ^{48}V was separated, carrier-free, according to Irvine and Schindewolf.[3]

Counting techniques

Integral γ-counting was used for ^{187}W and ^{48}V using a well-type NaI(Tl) detector. Because the daughter ^{99}Te interferes with γ-counting of ^{99}Mo, β-counting with an end-window G.M. tube was used for ^{99}Mo after separation as MoS_3.

Homogeneous precipitation of tungsten

Upon acidifying a standardised sodium tungstate solution with a mineral acid, incomplete precipitation of tungstic acid occurs. The resulting precipitate can be redissolved by adding an adequate amount of hydrogen peroxide, a soluble peroxy-acid being formed.

When this solution is heated, the excess of hydrogen peroxide and the peroxytungstic acid are decomposed, causing a homogeneous precipitation of tungstic acid.

Preliminary experiments showed that, in HNO_3 medium, optimum results were obtained by adding an equal volume of HNO_3 (60%) to the aqueous solution of the tungstate, and by redissolving the

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precipitate with 1 ml of H_2O_2 (30%). Thermal decomposition took place on heating the solution at 60° for 90 min, after which the precipitation was complete.

Homogeneous precipitation from other mineral acid solutions is less successful. Thermal decomposition in an $HClO_4$ medium, for instance, proceeded very slowly in the presence of large amounts of $HClO_4$, so that only 5 ml of $HClO_4$ (70%) could be used per 25 ml of tungsten solution. Even then a heating period of 2 hr at 80° was required before the decomposition was complete.

The decomposition in H_2SO_4 (10 ml of 98% acid per 25 ml of tungsten solution) also proceeded slowly, so that a temperature of 110° was necessary during 4 hr.

In all the experiments the amount of tungsten left in solution was computed by adding, before the acid, 500 μl of ^{187}W tracer of known activity (approx. 1 × 10^6 cpm) and counting an aliquot of the filtrate.

The results are summarised in Table I. Results by precipitation with cinchonine and β-naphthoquinoline are included for comparison.

TABLE I.—QUANTITATIVE CHARACTER OF THE TUNGSTEN PRECIPITATION

W/25 ml, *mg*	Tungsten left in solution, %*				
	HNO_3	$HClO_4$	H_2SO_4	Cinchonine	β-naphthoquinoline
251·08	0·13	0·60	4·03	0·44	0·13
100·5^6	0·11^5	0·91	6·39	0·37	0·47
50·9^9	0·10	0·72	4·87	1·42	0·96
20·8^7	0·51	1·40	13·76	1·37	3·38
10·8^3	0·66^5	1·90	18·13	4·82	5·33

* Average of 2 experiments.

From Table I it appears that homogeneous precipitation of tungsten from a nitric acid solution gives highly satisfactory tungsten recoveries. At the highest tungsten concentrations investigated, the recovery is identical to that with β-naphthoquinoline whereas at low concentrations, the former proves to be far superior (99·34% instead of 95%).

Homogeneous precipitation from a perchloric acid medium is somewhat less satisfactory, although it is still superior to precipitation with the organic reagents.

Homogeneous precipitation from a sulphuric acid medium, on the other hand, is unacceptable. Losses of up to 20% occur at the higher dilutions investigated.

Co-precipitation of molybdenum and vanadium

It is well known that in the presence of molybdate and vanadate, large amounts of Mo and V co-precipitate with tungstic acid. It might be expected that homogeneous precipitation would reduce this co-precipitation to a considerable extent.

Conditions for minimum co-precipitation of molybdenum were examined by varying the temperature, and consequently the decomposition rate of the peroxytungstate. In all the experiments the amount of molybdenum co-precipitated was determined by measuring the ^{99}Mo activity left in solution.

The results for solutions containing 50 mg of tungsten (as tungstate) and 15 mg of molybdate are summarised in Fig. 1.

It appears that the co-precipitation increases if a decomposition temperature higher than 60° is chosen. The experiments showed that at this temperature a heating period of 1·5 hr is required to achieve complete thermal decomposition of the peroxytungstate.

The co-precipitation of molybdenum was investigated for molybdenum/tungsten

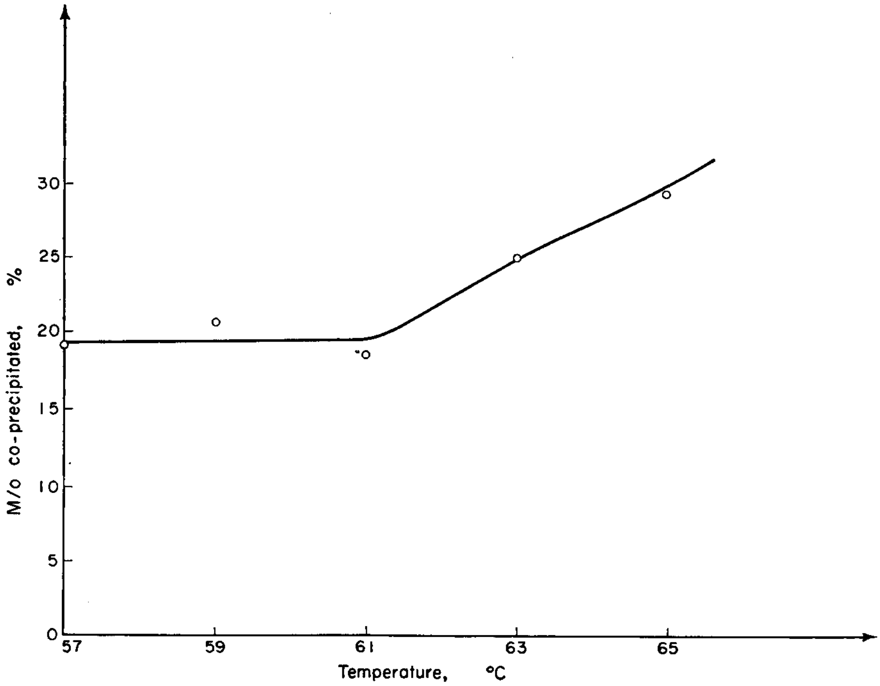

FIG. 1.—Molybdenum co-precipitated as a function of temperature.

ratios varying from $3{\cdot}5 \times 10^{-3}$ to 1×10^{2}; the vanadium/tungsten ratio was varied from $1{\cdot}6 \times 10^{-3}$ to 50. The absolute amount of tungsten precipitated varied between 251 mg for small ratios, down to 5 mg for larger ratios.

The results for molybdenum are summarised in Table II.

Results for the co-precipitation of molybdenum using β-naphthoquinoline are given by Leliaert (*loc. cit.*) and are presented for comparison in Table III.

It is apparent that the co-precipitation of molybdenum is reduced to a considerable

TABLE II. CO-PRECIPITATION OF MOLYBDENUM
(homogeneous precipitation)

W, *mg*	Mo, *mg*	Mo/W ratio	Mo co-precipitated, %	Error on W, %
251	0·64	$3{\cdot}53 \times 10^{-3}$	93·3	0·28
251	1·25	$4{\cdot}95 \times 10^{-3}$	88·2	0·53
251	2·22	$9{\cdot}10 \times 10^{-3}$	90·0	0·95
251	5·15	$2{\cdot}08 \times 10^{-2}$	90·6	2·22
251	10·3	$4{\cdot}18 \times 10^{-2}$	73·9	3·62
251	22·2	$8{\cdot}85 \times 10^{-2}$	49·0	5·16
50·1	11·2	$2{\cdot}25 \times 10^{-1}$	27·9	7·35
50·1	22·2	$4{\cdot}5 \times 10^{-1}$	22·9	12·0
10·0[2]	12·5	1·25	12·4	17·10
5·0[1]	52·3	$1{\cdot}04 \times 10$	9	—
5·0[1]	502	$1{\cdot}01 \times 10^{2}$	3·2	—

extent, although the induced error is far from negligible in the case of large Mo-W ratios.

The co-precipitation of vanadium was studied in the same experimental conditions as for molybdenum, using ^{48}V tracer. The results as summarised in Table IV, the data given by Leliaert using β-naphthoquinoline being presented in Table V.

TABLE III.—CO-PRECIPITATION OF MOLYBDENUM
(β-naphthoquinoline procedure)

Mo/W ratio	Mo co-precipitated, %
0·15	80
0·3	65
1·17	32
2·35	26

TABLE IV.—CO-PRECIPITATION OF VANADIUM
(homogeneous precipitation)

W, *mg*	Mo, *mg*	V/W ratio	V co-precipitated %	error on W, %
251	0·40	1·6 × 10^{-3}	5·8	0·02
251	1·00	4 × 10^{-3}	5·2	0·03
251	2·00	8 × 10^{-3}	4·8	0·05
251	5·00	2 × 10^{-2}	4·5	0·13
251	10·0	4 × 10^{-2}	4·3	0·24
251	20·0	8 × 10^{-2}	3·8	0·43
251	50·0	2 × 10^{-1}	2·7	0·76
100·2	50·0	5 × 10^{-1}	1·6	1·05
100·2	100	1	1·1	1·44
50·1	250	5	0·35	2·4
5·0^{1}	250	5·0 × 10^{1}	less than 0·3	less than 20

TABLE V.
CO-PRECIPITATION OF VANADIUM
(β-naphthoquinoline)

V/W ratio	V co-precipitated, %
0·01	10
0·1	7·5
0·2	7
0·5	5·2
1·0	3·5
2·0	2·8

It is apparent that the vanadium co-precipitation is also considerably reduced by homogeneous precipitation, and is smaller than the co-precipitation of molybdenum by an order of magnitude.

Determination of the distribution coefficients

It is well known that in co-precipitation phenomena three types of distribution occur between solid and liquid phase. Linear distribution following Nernst's law can occur according to equation (1):

$$\frac{x}{a-x} = D\frac{y}{b-y} \qquad (1)$$

where x and y represent the respective amounts of carrier and co-precipitant separated, a and b the initial concentrations.[4]

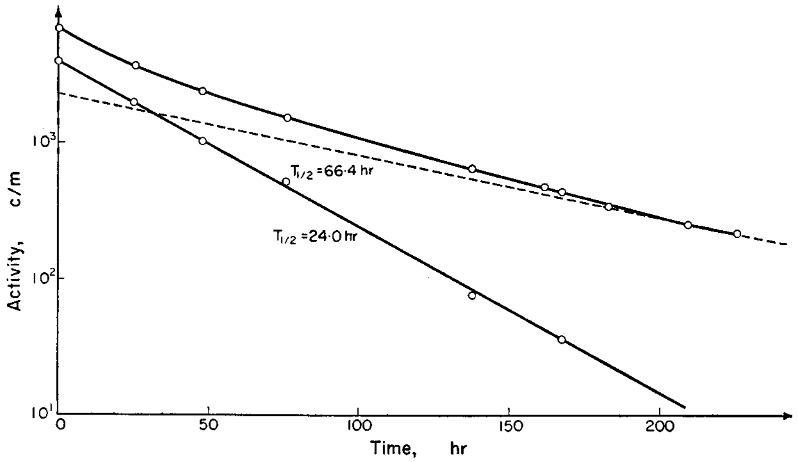

FIG. 2.—Analysis of ^{187}W–^{99}Mo decay curve.

In the second case Doerner and Hoskins[5] law is observed, following the logarithmic distribution of equation (2):

$$\ln\frac{a}{a-x} = \lambda\,.\,\ln\frac{b}{b-y} \qquad (2)$$

In the third case the amount of co-precipitant is linear with the amount of precipitated carrier. This type of distribution was first observed by R. Mumbrauer,[6] and a quantitative interpretation of it was given by Hahn,[7] while the distribution law was deduced by Riehl[8] to be equation (3):

$$\frac{x}{y} = K\,.\,\frac{a}{b} \qquad (3)$$

In the present case, tracer techniques offer a relatively simple means of determining the amount of co-precipitant as a function of the amount of precipitated carrier. To effect this, a small quantity of solution was removed at regular intervals. Since the half-lives of ^{187}W and of ^{99}Mo or ^{48}V are sufficiently different, the amount present of each element may be computed by analysis of the composite decay curve, after extrapolation to time t_0

Typical decay curves are given in Figs. 2 and 3.

Procedure: In a 400 ml conical flask are placed successively 100 ml of tungstate solution (10 mg of W/ml), 1 ml of molybdate (10 mg of Mo/ml) or 1 ml of vanadate (2 mg of V/ml), 100 ml of HNO_3 (60%), 5 ml of H_2O_2 (30%), 4 ml of ^{187}W tracer and 4 ml of ^{99}V tracer. The activities of the tracer solutions were chosen to correspond to approximately $1{\cdot}5 \times 10^5$ cpm of each tracer in the Mo co-precipitation experiments, and $1{\cdot}7 \times 10^6$ cpm in the case of V.

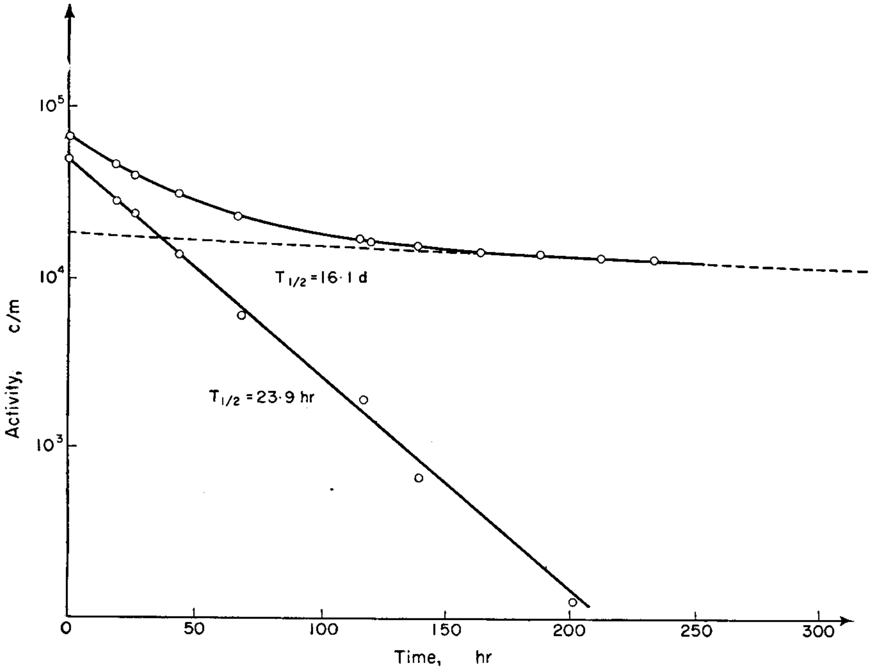

FIG. 3.—Analysis of ^{187}W–^{48}V decay curve.

The solution was heated in a thermostat at 60° and 5 ml portions of solution were removed by reverse filtration through an asbestos filter at 5-min intervals.

In the case of molybdenum, the isotopes are measured by G.M. counting, to avoid interference from ^{99}Tc daughter activity. The filtrates were therefore diluted to 50 ml, neutralised to pH2 with ammonia, and precipitated as their sulphides with thioacetamide, and the collected sulphides were mounted on standard planchettes and measured with the G.M. counter.

In the case of vanadium, 4 ml of the filtrates were counted in standard vials in a well-type NaI(Tl) detector.

The results are presented in Fig. 4, curve 1 (Mo) and curve 2 (V).

The values of D, λ and K computed according to equations (1), (2) or (3) are represented in Table VI.

From Table VI it appears that Riehl's law is followed in both cases; the amounts of co-precipitants are directly proportional to the amounts of precipitated carrier, the mean values being $K_{Mo} = 1{\cdot}34\ (\pm 0{\cdot}09)$ and $K_V = 14{\cdot}4\ (\pm 2{\cdot}6)$.

According to the views of Hahn this type of distribution does not involve true homogeneous mixed crystal formation, the process rather being caused by surface layer crystallisation, with continuous diffusion from the solution into the crystal body.

TABLE VI.—CO-PRECIPITATION OF MOLYBDENUM WITH TUNGSTEN

W pptd, %	Mo co-pptd, %	Distribution coefficients		
		D	λ	K
17·4	13·4	0·73	0·75	1·30
27·3	21·2	0·72	0·75	1·29
29·0	24·1	0·78	0·80	1·20
44·2	27·2	0·47	0·55	1·62
54·1	34·1	0·44	0·54	1·48
58·2	43·2	0·55	0·65	1·35
70·1	54·1	0·50	0·65	1·30
80·2	60·8	0·38	0·58	1·32
90·1	69·7	0·26	0·58	1·29
90·8	76·4	0·33	0·69	1·20

CO-PRECIPITATION OF VANADIUM WITH TUNGSTEN

W pptd, %	V co-pptd, %	Distribution coefficients		
		$D \times 10^2$	$\lambda \times 10^2$	K
25·6	2·1	6·2	7·1	12·1
30·3	2·2	5·2	6·0	13·7
41·2	3·9	5·8	7·5	10·5
42·5^{5}	2·3	3·2	7·1	18·5
43·1	4·0	5·5	7·2	10·8
54·7	4·4	3·8	5·7	12·4
63·7	4·0	2·4	4·0	15·9
77·8	4·2	1·3	2·9	18·5
88·7	4·9	0·7	2·3	18·1
92·1	6·1	0·5^{6}	2·1	15·1
92·8	7·5	0·6^{3}	3·0	12·4

Determination of tungsten in alloy steels

The determination of tungsten by homogeneous precipitation was tested on a number of N.B.S. and British Standard Steels. The results obtained were corrected for incomplete tungstic acid recovery (Table I), silicon content (given by the certificates), molybdenum and vanadium content (Table II and III respectively). Double homogeneous precipitation was used for Mo-W ratios larger than unity.

Procedure: A suitable amount of steel turnings (1–2 g) is treated with 30 ml of 11*N* HCl in a 400-ml beaker. The solution is heated on a hot plate below the boiling point until the reaction subsides, Then 20 ml of 14*N* HNO_3 are added dropwise. If tungsten carbide particles remain undissolved, 10 ml of $HClO_4$ (70%) are added and the solution is taken to near dryness. The residue is treated with 25 ml of 14*N* HNO_3 and is again taken to dryness, and the process is repeated to insure a complete removal of the hydrochloric acid. The residue is treated with 50 ml of water, 2 ml of H_2O_2 (30%) and 50 ml of 14*N*HNO_3. If large amounts of silica are present, the insoluble residue is removed by filtration and the silicon correction is not applied. The solution is heated in a thermostat at 60° for 1·5 hr. As soon as the precipitate has settled, the hot solution is filtered (fine porosity paper), washed with hot 1% HNO_3 and incinerated at 800° for 1 hr.

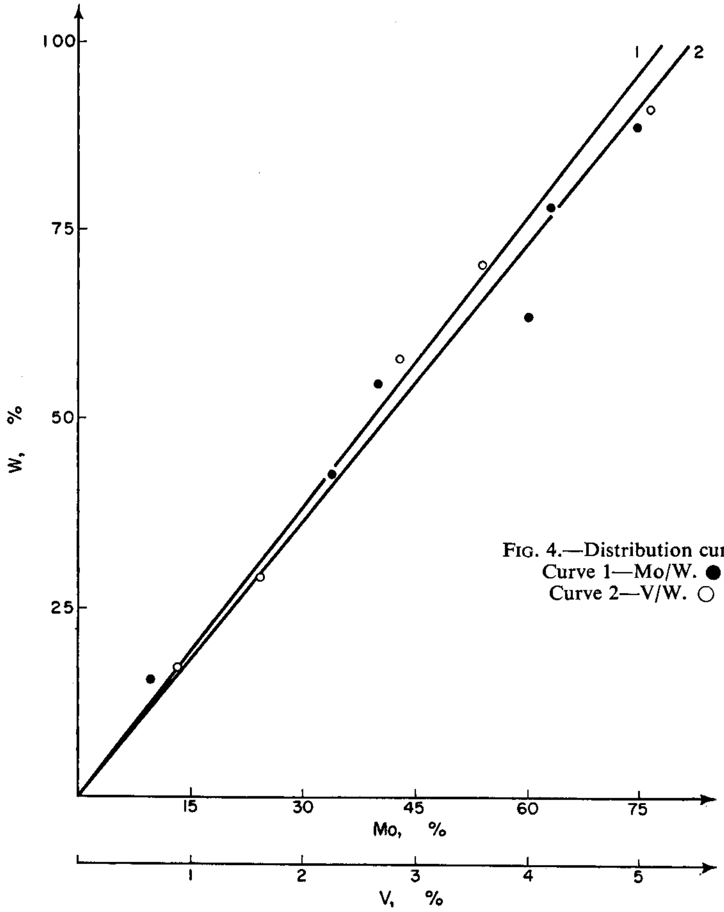

FIG. 4.—Distribution curves.
Curve 1—Mo/W. ●
Curve 2—V/W. ○

TABLE VII.—DETERMINATION OF TUNGSTEN IN STANDARD STEELS

N.B.S steels	W, %	Stand. deviation,* %	Mo/W ratio	Sample size, g	W after 1st precipitation, %	W after 2nd precipitation,	Mean, %	W after correction, %	Deviation from certificate, %
153	1·58	1·5	5·2	2·0015 2·0009	— —	1·54^{1} 1·58^{1}	1·56^{1}	1·56^{4}	−1·0
132A	6·20	1·1	0·73	2·0023 2·0006	7·23 7·19	— —	7·21	6·17^{5}	−0·4
155	0·517	1·3	0·075	2·0038 2·0006	0·526 0·524	— —	0·525	0·505	−2·4
50 C	18·44	0·4	0·0044	1·0094 1·0008 1·0012	18·93 18·82 18·88	— — —	18·88	18·30	−0·7^{5}
Tool steel 440/880	13·0	—	0·0054	1·5230 1·5024 1·5026	13.27 13·23 13·19	— — —	13·23	12·90	−0·7
B.C.S 241/1	19·61	0·4^{5}	0·026	1·0007 0·9992	20·16 20·25	— —	20·21	19·49	−0·6

* The standard deviation was computed from the values given in the respective certificates.

NBS 153: C 0·864; Mn 0·219; P 0·025; S 0·008; Si 0·187; Cu 0·099; Ni 0·107; Cr 4·14; V 1·04; Mo 8·39; W 1·58; Co 8·45•
NBS 132A: C 0·825; Mn 0·268; P 0·029; S 0·006; Si 0·190; Cu 0·120; Ni 0·137; Cr 4·21; V 1·94; Mo 4·51; W 6·20.
NBS 155: C 905; Mn 1·25; P 0·015; S 0·010; Si 0·322; Cu 0·083; Ni 0·100; Cr 0·485; V 0·014; Mo 0·039; W 0·517.
NBS 50C: N 0·012; As 0·022; Sn 0·018; C 0·719; Mn 0·342; P 0·022; S 0·010, Si 0·311; Cu 0·079; Ni 0·069; Cr 4·13; Cr 4·13; V 1·16; Mo 0·082; W 18·44.
NBS Tool Steel: 440/880: C 0·7; Mn 0·15; Si 0·14; Cu 0·059; Cr 2·12; V 2·11; Mo 0·070; W 13·0; Co 11·8.
BCS 241/1: Sn 0·025; C 0·85; Mn 0·295; P 0·021; S 0·033; Si 0·33; Cu 0·10; Ni 0·075; Cr 5·03; V 1·57; Mo 0·52; W 19·61; Co 5·67.

The results are summarised in Table VII. From this it appears that the results are in good agreement with those of the certificates, the deviation from the given values being within 1 %, except for NBS steel No. 155. The larger deviation in this case is obviously caused by the fact that with a 2-g sample a precipitate of only 15 mg of WO_3 is obtained.

Zusammenfassung—Wolfram wird gravimetrisch bestimmt, nach Fällen aus homogener Lösung durch thermische Zersetzung des löslichen Peroxywolframates in Salpetersäure-Wasserstoffperoxyd-Lösung. Es scheint, dass in allen Fällen, besonders für niedere Konzentrationen, die neue Methode den klassischen Verfahren unter Verwendung von Cinchonin oder β-Naphthochinolin überlegen ist. Weiters is die Mitfällung von Molybdän und Vanadin beträchtlich reduziert. Mitfällungsstudien zeigten, dass die Verteilungsfaktoren für beide Verunreinigungen ein lineares Verhalten aufweisen. Die Methode wurde an einer Anzahl von Standardstählen erprobt, wobei für Unvollständigkeit der Fällung und Mitfällung von Verunreinigungen Korrekturen angebracht wurden, deren Grösse aus experimentellen Befunden erhalten werden konnte. Die Resultate waren sehr zufriedenstellend.

Résumé—Les auteurs ont mis au point une méthode de précipitation homogène pour le dosage gravimétrique du tungstène, par décomposition thermique de peroxytungstate soluble obtenu à partir d'une solution acide nitrique-eau oxygénée. Il apparaît que dans tous les cas, et spécialement pour de faibles concentrations, la récupération du tungstène est supérieure à celle obtenue par les techniques classiques utilisant la cinchonine ou la β-naphtoquinoleine. De plus, la coprécipitation du molybdène et du vanadium est concidérablement réduite. L'étude du processus de coprécipitation a montré que les coefficients de partage suivent une loi linéaire pour les deux impuretés. La méthode a été essayée, donnant de bons résultats, sur un certain nombre d'aciers spéciaux standard au tungstène; les corrections de précipitation incompléte et de coprécipitation, basées sur les valeurs expérimentales, ont été appliquées.

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ANALYTICAL USE OF ARSENAZO III

DETERMINATION OF THORIUM, ZIRCONIUM, URANIUM AND RARE EARTH ELEMENTS

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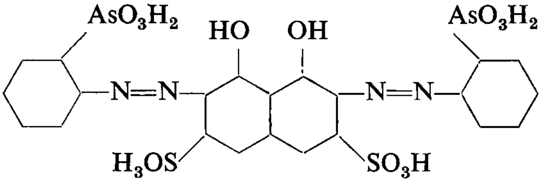
Summary—The reagent arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-phenylarsonic acid]) gives marked colour reactions with a number of elements. Anions affect the reaction only to a slight degree and it is possible to work at low pH values; the reaction is very sensitive and the compound can thus be used for the photometric determination of Th, Zr, Hf, U, rare earths, and some other elements. The method is most selective for Th, Zr and U^{IV}. Materials containing these elements can be analysed directly, in the solutions formed after dissolving the sample, without separation of the stable elements.

AZO-DYES based on chromotropic acid are widely used as reagents for the photometric determination of various elements. Especially useful and universally applicable are reagents containing the arsonous group-AsO_3H_2. Such a reagent was first prepared by Kuznetsov[1] in 1941 and named, in its abbreviated form, "arsenazo". Various improved analogues of arsenazo were sythesised later and also tested; these included arsenazo II (which is a double molecule of arsenazo)[2] and arsenazo III, a bis-diazo dye based on chromotropic acid and *o*-aminophenylarsonic acid.[3] The latter compound, 1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-phenylarsonic acid], is especially suitable for the photometric determination of thorium, zirconium, uranium^{IV} and of some other elements.



ARSENAZO III

The properties of arsenazo III

Arsenazo III is generally obtained in the form of its disodium salt; it is a crystalline, dark-red powder, soluble in water or in weak acids, readily soluble in water which has been rendered alkaline with sodium bicarbonate or sodium carbonate, and insoluble in concentrated acids, or in solutions saturated with sodium chloride, acetone, alcohol or ethyl ether. The reagent is stable in its dry as well as in its dissolved form; its properties do not change even when stored for long periods. Oxidising agents (H_2O_2, Cl_2, Br_2) and strong reducing agents ($Na_2S_2O_3$, Ti^{III}) attack the reagent; therefore solutions in which the elements are to be determined must be freed of oxidising and reducing agents. Usually this does not present any serious difficulties.

The colour of the aqueous solutions of arsenazo III depends on the pH of the medium. The solutions are pinkish or red-crimson coloured, depending on the concentration, within the pH limits of 4 to 10*N* hydrochloric acid, *i.e.* under conditions usual for the determination of most elements; a 0.01–0.1% aqueous solution of arsenazo III is generally used. In the alkaline region, at pH 5 and higher, a violet or blue colour is observed; the colour is green in concentrated sulphuric acid.

Colour reactions with elements

Colour reactions of arsenazo III at various acidities conform to the general rules for the effect of the pH on the colour of the reaction products obtained with colour reagents.[4] Arsenazo III gives colour reactions with many elements (Table I). Its basic characteristic property consists in its ability to form stable chelates; elements can therefore be determined in strongly acidic media and in the presence of sulphates, fluorides, phosphates, oxalates and other complex-forming anions which generally inhibit the direct determination of elements.

TABLE I.—COLOUR REACTIONS OF ARSENAZO III

Element	Conditions of determination	Colour of complex	Elements inhibiting the determination
Reagent alone	4–10*N* HCl	Pinkish–crimson	
Th	0·01–10*N* HCl	Green	—*
U^{IV}	0·05–10*N* HCl	Green	Th*
Zr	0·2–10*N* HCl	Green	Th
UO_2^{2+}	pH 4–pH 1	Green	Zr, rare earths, Ca†
Sc	pH 4–pH 1	Violet	Th, Zr, U, Ca, Cu,
Y, La and lanthanides	pH 4–pH 3	Green	Th, Zr, U, Ca, Cu,
Bi	pH 4·5–pH 1·5	Violet–blue	Many elements‡
Pb	pH 5–pH 4	Blue	Many elements‡
Fe^{III}	pH 3–pH 1·5	Lilac–violet	Many elements‡
Cu	pH 5–pH 4	Blue	Many elements‡
Ba	pH 5–pH 4·5	Violet–blue	Many elements‡
Ca	pH 5–pH 4	Blue	Many elements‡

* In the presence of oxalic acid for masking zirconium.
† In the presence of Trilon B and potassium fluoride, for masking thorium and other elements.
‡ The possibility of selective determination of these elements was not investigated in detail.

Photometric determinations in strongly acidic media are useful in many cases; difficulties caused by the partial hydrolysis of ions of the elements to be determined are eliminated; it is no longer necessary to maintain carefully the pH with the aid of buffer solutions; the selectivity of determination is increased for a number of elements, *etc.* The slight effect of anions makes it possible to use direct methods of determination in many cases, *i.e.* direct photometric determination can be carried out without separating sulphates, phosphates and other admixtures.

The sensitivity of the colour reactions is of a sufficiently high degree (0.05 to 0.01 μg/ml of the element) when using a spectrophotometer or a photocolorimeter. Quantities of 0.5 μg/ml or more of the element can be determined by visual methods. The methods are most sensitive for the determination of thorium, zirconium, uranium, the rare earth elements and less sensitive for lead, bismuth, iron, copper, calcium, barium.

The high selectivity of the colour reactions is coupled with a well defined contrast in colour transition from pinkish (reagent) to blue or even emerald green (complexes of arsenazo III with elements) and with a high stability of the corresponding arsenazo III complexes; this makes it possible to attain high degrees of dilution without dissociation of the complex. The form of the curves—absorption spectra of the reagent and the complex—is especially important when using photometers. A considerable shift of the absorption spectrum of the complex is observed towards the long wavelengths (compared to the absorption spectrum of the reagent) as well as two sharply defined peaks on the curve of the light-absorbing complex (Fig. 1); this phenomenon makes it possible to attain maximum sensitivity during the determination of the element when working at the optimum wavelengths of 660 to 665 mμ. Furthermore, the reagent itself, present in considerable excess during the determination, does not influence the reaction when using this wavelength. A red-light filter is generally used when working

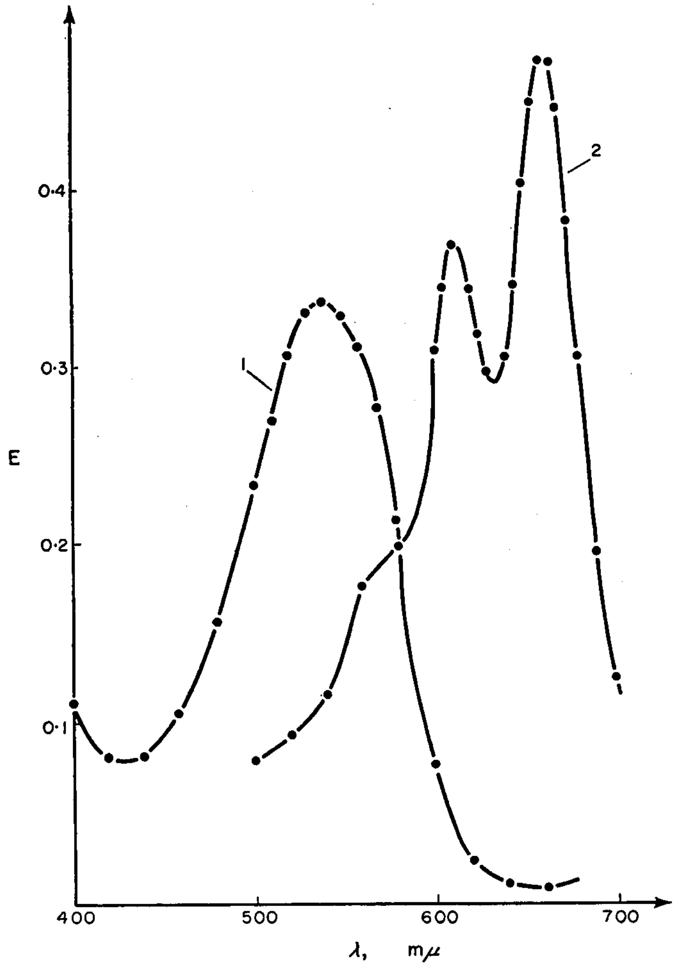


FIG. 1.—Absorption spectrum of arsenazo III and of its thorium complex:
1. 0·9 × $10^{-5}M$ arsenazo III in 4N HCl;
2. 0·9 × $10^{-5}M$ arsenazo III and 2·5 × $10^{-5}M$ $Th(NO_3)_4$ in 4N HCl;
(Spectrophotometer SF–4, 10 mm cell).

with photocolorimeters; in this case the excess reagent is eliminated almost completely. The coefficients of molar extinction of some systems are listed in Table II.

TABLE II.—SENSITIVITY OF COLOUR REACTIONS OF ARSENAZO III

Element	Conditions of max. sensitivity of reaction	Coefficient of molar extinction, ε*	Sensitivity, $\mu g/ml$	
			Spectrophotometer, 50 mm cell	Visual
Th	9*N* HCl, λ 665 mμ	130,000	0·01–0·02	0·5–1
Zr	9*N* HCl λ 665 mμ	120,000	0·01–0·02	0·5–1
Hf	9*N* HCl λ 665 mμ	~95,000	0·02	1–2
U^{IV}	4*N* HCl λ 670 mμ	100,000	0·02	1–2
UO_2^{2+}	pH 2·0 λ 665 mμ	53,000	0·02	1–2
Sc	pH 1·7 λ 675 mμ	19,000	0·05	3–4
Y	pH 3·0 λ 655 mμ	55,000	0·02	1–2
La	pH 3·0 λ 655 mμ	45,000	0·02	1–2
Ce	pH 3·0 λ 655 mμ	47,000	0·02	1–2
Gd	pH 3·0 λ 655 mμ	58,000	0·02	1–2
Tb	pH 3·0 λ 655 mμ	62,000	0·02	1–2
Yb	pH 3·0 λ 655 mμ	49,000	0·02	1–2
Zn	pH 3·0 λ 655 mμ	43,000	0·02	1–2
Ca	pH 5·0 λ 655 mμ	~10,000	0·05–0·1	3–5
Pb	pH 5·0 λ 655 mμ	10,000	0·05–0·1	3–5

* Calculated according to the formula $\varepsilon = \frac{E}{cl}$. The method of saturation at excess reagent was used (*cf. e.g.* Fig. 4). For rare earths, data according to [15].

Selectivity

Arsenazo III (Table I) gives colour reactions with many elements and, consequently is not specific for any element.

Its selectivity, *i.e.* to determine any element in the presence of others, can therefore only be increased by using specific methods. The simplest method appears to be the determination of the required acidity of the solution.

The region of optimum pH values for the interaction of organic colour reagents with elements is known to vary for various elements. The distinct analogy between colour reactions and hydrolysis reactions should be noted.[5] Thus colour reactions with colour reagents are given in strongly acidic media only by those elements whose ions readily tend to hydrolyse: zirconium, hafnium, uranium^{IV}, thorium; in mildly acidic media the reactions also yield colours with iron^{III}, uranyl ion, rare earths; in mildly acidic media and in neutral media only with: calcium, strontium, magnesium.

Finally, the reaction conditions (optimum pH) are directly related and depend on the nature of the reagents used in the reaction. But for each reagent the ratio of optimum pH values of the reaction with elements remains always constant: easily hydrolysed elements interact in a very acidic medium, stable elements in less acidic media. This also holds true for the reagent arsenazo III.

It can be seen that a high degree of selectivity is attained when determining quadrivalent elements—zirconium, hafnium, thorium, uranium^{IV}—with arsenazo III; this reaction can be carried out in strongly acidic media, of the order of 2–10*N* hydrochloric acid ; stable elements do not inhibit the reaction. But the determination of uranium^{VI}, rare earths and of other elements is inhibited by many elements.

The degree of selectivity can also be increased by other methods apart from varying the acidity of the mixture. Frequently it is recommended to bind the inhibitors into a colourless stable complex. This is only possible when the element to be determined and the admixtures form with the masking, complex-forming compound—under the the given conditions (at defined pH)—complexes which differ markedly in their stability.

The system uranyl ion-Trilon B-stable elements is well-known. Oxalic acid is very useful when determining thorium in the presence of zirconium; the oxalic acid binds the zirconium and has practically no masking effect on the thorium (in a 3–9*N* hydrochloric acid medium). Fluorides, at pH 2, bind thorium almost completely and do not inhibit the colour reaction of uranyl ion with arsenazo III. Other selective masking, complex-forming compounds can, no doubt, be found.

The selectivity can also be increased by utilising the so-called extraction-photometric methods for the determination of elements; these methods have been described in recent publications.[6,7] It has been shown that complexes of arsenazo III and elements can be extracted with butyl or amyl alcohol when salts of a heavy organic cation, *e.g.* diphenylguanidine chloride, are introduced into the solution. In this case direct photometric determination is carried out in the organic phase, without re-extraction. Thus the determination is combined with the simultaneous separation from other, non-extracted elements. The extraction-photometric methods have been investigated for uranium[7] and thorium.[6] They have also been used for zirconium and rare earths but in this case it is preferable to employ more hydrophobic analogues of arsenazo III, *e.g.* tetrabromo-arsenazo III, which is 1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-4,6-dibromophenylarsonic acid].

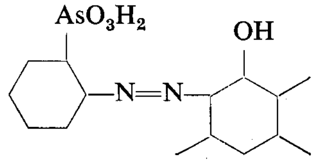
A high degree of selectivity can be achieved by combining these methods for the determination of thorium, zirconium, hafnium, and uranium$^{IV\&VI}$. When analysing substances containing large or average concentrations of the above-named elements it is possible to carry out direct determinations in the solutions obtained after decomposing these substances, without separation of the admixtures. Preliminary concentration is required during the analysis of rock-samples and of other materials containing small amounts of the elements. This is achieved by a one-stage precipitation reaction,[8,9] a single-stage extraction,[7] or similar comparatively simple methods. Complete separation of the admixtures is not necessary—this facilitates the method considerably.

The selectivity is also influenced by a larger or smaller excess of reagent used during the photometric determination. In the latter case, *i.e.* when the reagent is present in not too large a molar excess with regard to the element to be determined (two-to-three-fold), it will be observed that the degree of selectivity is increased.

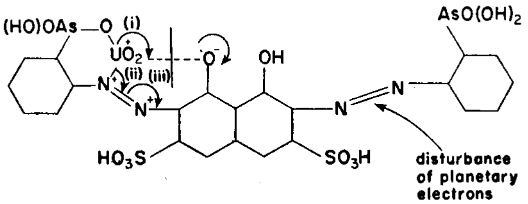
Complex-formation of arsenazo III *with elements*

Arsenazo III forms 1:1 complexes with 2+ and 3+ charged cations of elements, *e.g.* Sr, UO_2^{2+}, ZrO^{2+} or La. With 4+ charged cations, *e.g.* Th, Zr, Hf, U^{IV}, the composition may be related to the conditions (pH and the ratio of the components) and E:R=1:1 or E:R=1:2. The composition of complexes of 4+ charged elements is always in the ratio 1:2 under the conditions for colour reactions, when the reagent is present in large excess.

The structure of the complex and the reasons for its unusually high stability will be described in future communications. It should be noted here that although arsenazo III contains two functional groups:



only one of these groups partakes in the complex-formation with elements. The structure of the complex of uranium^{VI} with arsenazo III, for example, can be depicted as follows:



METHODS FOR THE DETERMINATION OF ELEMENTS

Thorium

The method is perhaps most selective for the determination of thorium. Stable elements do not inhibit the reaction if the ratio of thorium to elements is not in excess of: Zr—1:1,000; UO_2^{2+}—1:6; rare earths (Ce-subgroup)—1:50; rare earths (Y-subgroup)—1:100; Ti—1:10; Cr^{III}—1:200; Ni—1:500; Fe^{III}, Pb, Co, Ca, Al and other elements—1:1,000 to 5,000. It was previously pointed out that zirconium can be masked effectively by oxalic acid and that uranium^{IV} readily oxidises to uranium^{VI}. Zirconium is masked most effectively in a 2.5–3.0*N* hydrochloric acid medium. For every 25 ml of the final solution one has to introduce 6 ml of hydrochloric acid (sp. gr. 1.19), 10 ml of 4% oxalic acid solution and 0.5 ml of a 0.1% aqueous solution of arsenazo III during the photometric determinations. The content of thorium should be 1–25 μg.[9] The measurements are carried out with a spectrophotometer at 665 mμ or with a photocolorimeter with a red-light filter. The effect of the acidity on the colour-formation of the thorium arsenazo III complex is shown in Fig. 2.

The methods for the determination of thorium in various substances can be used for the direct determination of thorium as well as for samples with a low thorium-content, after preliminary separation of the admixtures.[3,6,8–10]

The following procedure may be adopted when analysing rock samples:[9]

Decompose 0·1–0·5 g of the sample, containing 0·0001% and higher quantities of thorium, supposedly containing 1–25 μg of thorium, with hydrofluoric acid. Evaporate, treat the residue with hydrofluoric acid and wash with water. After filtering, transfer the precipitate to a platinum dish and treat with perchloric acid + hydrochloric acid. After evaporating, dissolve the residue in 1·6 ml of hydrochloric acid (1:1) + 5 ml of water and transfer to a 25-ml volumetric flask. Add ascorbic acid to reduce the iron^{III} and 10 ml of 4% oxalic acid solution in hydrochloric acid (1:1), 0·5 ml of a 0·1% solution of arsenazo III and dilute to the mark with water. The photometric determination is carried out on a FEK–M with a red-light filter or on a SF–4 at 665 mμ in 50-mm cells. The thorium content is found via a calibration curve. Six to 8 determinations can be carried out in 6 hr.

The determination of thorium is not inhibited by substantial quantities of niobium. Thus it is possible to carry out direct determinations of thorium in niobium concentrates after dissolving the sample, without preliminary separation of niobium.[10] Analysis conditions are essentially identical to those described above.

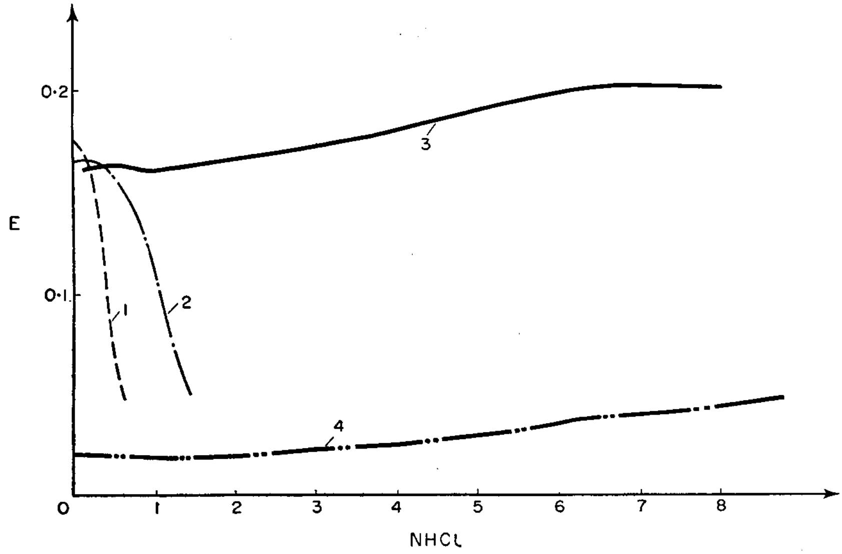


FIG. 2.—Effect of pH on the colour of the thorium complexes with the various reagents:
1. Arsenazo I, conc. Th–1·2 × $10^{-5}M$, 650 mμ;
2. Arsenazo II, conc. Th–1·2 × $10^{-5}M$, 600 mμ;
3. Arsenazo III. conc. Th–0·4 × $10^{-5}M$, 665 mμ;
4. Arsenazo III., concentration of the reagents 0·5 × $10^{-4}M$.

Uranium

The method for the determination of quadrivalent uranium with arsenazo III is considerably more selective than for the determination of uranium^{VI}. Preliminary reduction has to be carried out; this and the stability of uranium^{IV} may cause various difficulties; however, this method of determining uranium appears to be most satisfactory.[11] As in the case of thorium most cations and anions do not inhibit the reaction. Zirconium is masked by oxalic acid and iron^{III} is reduced with ascorbic acid. Only thorium causes substantial interference. The following analysis procedure may be used when the quantities of uranium and thorium are of the same order: up to the time of reduction of uranium only thorium is determined; after completion of the reduction the sum of thorium + uranium^{IV} is determined and the uranium content found from the difference.

The method of determination is as follows:[11]

Decompose 0·5 g of the rock sample, ore cake, *etc.*, containing 0·002% and larger quantities of uranium, by heating with hydrochloric acid + hydrogen peroxide. Dilute with 4*N* hydrochloric acid and filter into a 100-ml volumetric flask. Take two aliquots of 10 ml each and place in small flasks. Add 5–10 mg of ascorbic acid to both fractions (until discoloration of the brown colour of iron^{III} sets in) and to one fraction 5–6 granules of zinc (to reduce the uranium). Run off the solutions into 50-ml volumetric flasks, without transferring the zinc, and rinse out the flasks with 4*N* hydrochloric acid.

To each test sample add 2 ml of 4% oxalic acid solution, 2 ml of a 0·05% solution of arsenazo III and dilute to the mark with 4*N* hydrochloric acid. Photometric measurements are carried out at

665 mμ or on a photocolorimeter with a red-light filter in 20-mm cells, using the non-reduced aliquot as a standard.

The uranium content is found via a calibration curve: small volumes of the solution, containing, respectively 0, 4, 8, 15, 30 and 40 μg of uranium are subjected to the above procedures whilst maintaining accurately the degree of acidity, the period of reduction and other conditions.

The extraction-photometric method[7] can be used to achieve improved selectivity during the determination of sexavalent uranium.

Decompose a few mg of the sample, containing 1–50 μg of uranium, according to the mineralogical composition of the sample. After evaporation, treat the dry residue with 2·0 ml of 0·05*N* hydrochloric acid, 2·5 ml of a 5% solution of Trilon B, 1·00 ml of a 0·05% solution of arsenazo III, 0·5 ml of a 20% solution of diphenylguanidine chloride and add 5·00 ml of butanol. After extraction, transfer part of the upper layer to a 10-mm cell and evaluate photometrically, either on a spectrophotometer at 660 mμ or on a photocolorimeter with a red-light filter.

The uranium content is found via a calibration curve plotted in the manner described above.

Direct photometric determination without separation of the stable elements can be employed when determining uranium in pitchblende or in substances containing traces of admixtures. Sulphates, phosphates and even limited quantities of fluorides do not act as inhibitors. The photometric determination of uranyl ion is carried out at pH 1.5–3.5, and of uranium^{IV} in 3–9*N* hydrochloric acid.

Zirconium

The method is very selective for the determination of zirconium. In most cases, even during the determination of zirconium in complex samples, *e.g.* in ores,[12] and alloys based on copper, aluminium, magnesium and titanium, in the presence of niobium, tantalum and other elements,[13] it is not necessary to separate the stable elements or to concentrate the zirconium. Photometric measurements can be taken immediately after decomposing the sample. The complex of arsenazo III and zirconium is very stable and sulphates, phosphates and other anions have only a slight effect. Oxalates and fluorides mask zirconium. The sensitivity is approximately 0.01–0.05 μg/ml of zirconium (see Table II).

The effect of the acidity and the ratio of zirconium: arsenazo III on the intensity of coloration is shown in Figs. 3 and 4. The determination of zirconium can be carried out in strongly acidic media—from 2 to 11*N* hydrochloric acid *i.e.* under conditions where practically no hydrolysis or partial polymerisation of the zirconium cations occurs. This ensures very accurate results and good reproducibility of the analyses.

Goryushina and Romanova[12] showed that even in such complex samples as tin and titanium concentrates, magnesium fractions obtained on concentrating ores of various origin, *etc.*, direct photometric determination of zirconium can be carried out in solutions obtained after decomposing the substances, without preliminary separation of the stable elements:[12]

Fuse 0·1–0·2 g of the material in a platinum dish with 5 g of a mixture (1 : 1·5) of borax and sodium carbonate at 900°, for 7 to 10 min. After cooling, add boiling water and decant the liquid, with the residue of hydrates, into a beaker. Dilute the mixture with water to 150 ml and heat to achieve better coagulation. Filter off the residue, wash and dissolve in 2*N* hydrochloric acid. Aliquots containing 5 to 30 μg of zirconium are taken; to these are added 3 ml of a 1% gelatin solution, 1·00 ml of a 0·1% solution of arsenazo III and up to 50·0 ml of 2*N* hydrochloric acid. Photometric measurements are taken with a FEK–M, in a 2·0-cm cell, with a red-light filter. The zirconium-content is found via a calibration curve, plotted under identical conditions.

The concentration of 2*N* hydrochloric acid was selected on considering the most practical working conditions for the analysis of substances containing high or average concentrations of zirconium (0.1 % or more of zirconium). When the zirconium-content is low (0.01 % and less) determinations should be carried out in 9*N* hydrochloric acid. The only drawback is the relatively high volatility of hydrochloric acid. In some cases it may be more advantageous to work at acidities corresponding to the azeotropic composition of the system—hydrochloric acid 1:1(~6.1*N* hydrochloric acid.[14]

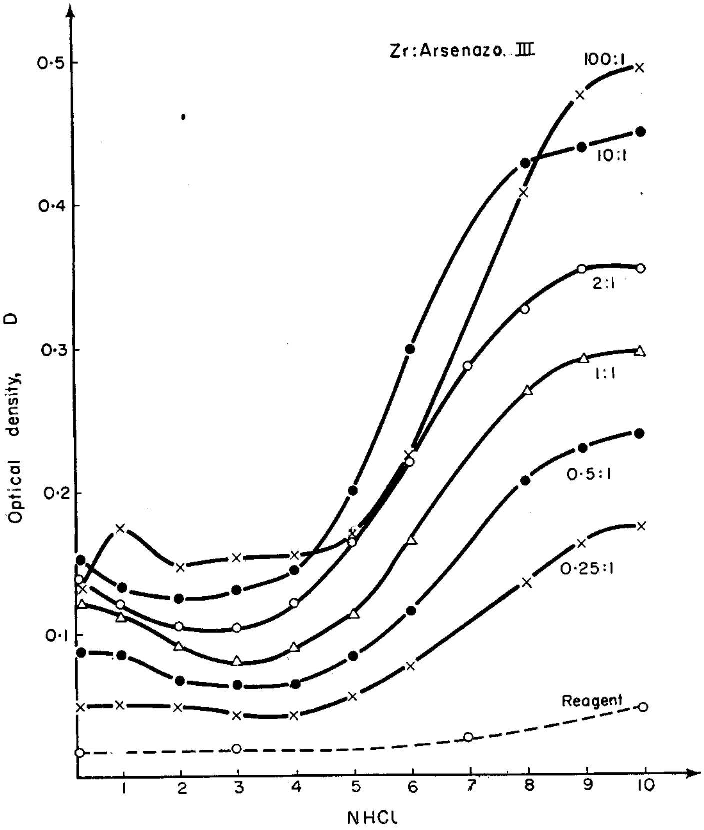


Fig. 3.—Effect of the concentration of hydrochloric acid and of the molar ratio of zirconium: reagent on the colour intensity (Concentration of arsenazo III: 0·9 $\times 10^{-5}M$, spectrophotometer SF–4, 665 mμ, 10-mm cell).

Zirconium must be concentrated when analysing alloys and substances containing zirconium in the form of admixtures (from 0.01 % to 0.0001 %). Titanium is known to be a very good co-precipitator for zirconium but its use has been proved inadvisable because it causes considerable interference when determining zirconium photometrically with reagents such as pyrocatechol violet, morin, phenylfluorone *etc.* These difficulties do not arise with arsenazo III. Titanium causes no interference even at ratios of zirconium:titanium = 1:1000. The determination of zirconium in aluminium–magnesium alloys is described as an example; it was investigated by Kuznetsov and the present author:

Weighed samples of the alloy (0·2–2 g), supposedly containing 2–40 μg of zirconium, are dissolved in 6*N* hydrochloric acid, to which nitric acid is added—to dissolve the copper.

Evaporate the samples to wet salts* and add 1 ml of a titanium solution containing 5 mg/ml of titanium, 5 ml 6*N* hydrochloric acid, then dilute with water to 50–100 ml.

Add 13 ml of 40% sodium acetate trihydrate solution. Check the acidity with universal indicator paper; the pH should be within the limits 2·0 to 2·5.

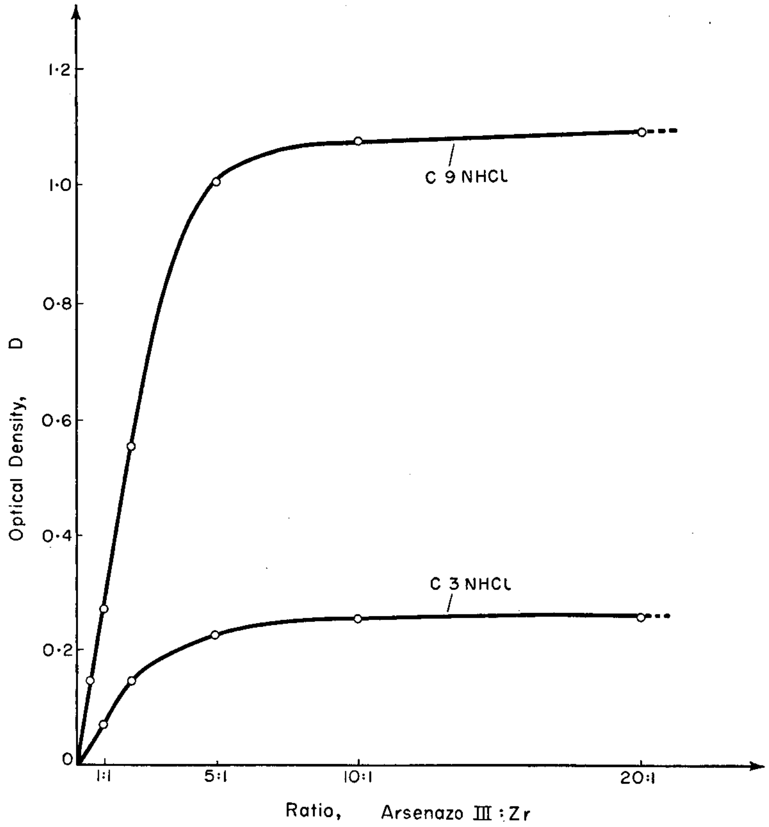


FIG. 4.—Effect of the molar ratio of reagent: zirconium on the colour intensity of the arsenazo III–zirconium complex (Concentration of zirconium: 0·9 × $10^{-5}M$, taken against water).

Maintain on a hot water bath for 30–60 min. The small quantity of flaky precipitate of titanium and zirconium hydroxides is filtered through a 7-cm diameter filter paper and washed with water.

Transfer the filter, together with the residue, into the same beaker in which the precipitation was carried out, add 10 ml of 6*N* hydrochloric acid and heat the mixture for 15–20 min whilst stirring with a small glass rod. A homogeneous paper pulp is formed and the solution is filtered into a 50-ml volumetric flask; the beaker and filter are washed 3 times with small quantities (2·5 to 3 ml) of 6*N* hydrochloric acid. It is necessary to allow the solution to drain off completely after each washing because the volume of 6*N* hydrochloric acid, which can be used for the washing is limited to 9–10 ml.

Add 1·00 ml of an arsenazo III solution, agitate the mixture, then add 30·0 ml of conc. hydrochloric acid (sp. gr. 1·18†) and dilute with 6*N* hydrochloric acid to the mark. Close the flask tightly to avoid losses in hydrochloric acid.

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* Evaporation to wet salts is not absolutely necessary. In this case the required pH of the solution is established, after diluting the solution, by using universal indicator paper or an internal indicator *e.g.* methyl violet, adding sodium acetate until the colour changes from blue to dark blue-violet.

† Use 28 ml when the sp. gr. of the conc. hydrochloric acid is 1·19, 32 ml for a sp. gr. of 1·17 and 34 ml for a sp. gr. of 1·16.

Photometric measurements are carried out on a spectrophotometer at 665 mμ, in a 10-mm cell, or on a photocolorimeter with a red-light filter, in a 20-mm cell. The solution of the No. 1 calibration curve is used as standard.

Calibration curve. Introduce into a series of 50-ml volumetric flasks: 0, 0·4, 0·8, 1·6, 4·0, 6·0 and 8·0 ml, respectively, of a zirconium solution in 6*N* hydrochloric acid containing 5 μg/ml of zirconium, a titanium solution in 6*N* hydrochloric acid, containing 5 mg/ml of titanium, 1·0 ml; a 0·25% solution of arsenazo III, 1·00 ml; conc. hydrochloric acid, 30 ml (sp. gr. 1·18); and dilute with 6*N* hydrochloric acid to the mark.

Note. Instead of 6*N* hydrochloric acid, azeotropic hydrochloric acid (∼6·1*N* hydrochloric acid) can be used, or a 1:1 solution of hydrochloric acid prepared from the conc. acid. In this case the calibration curve is plotted using the 1:1 acid.

Zirconium and hafnium

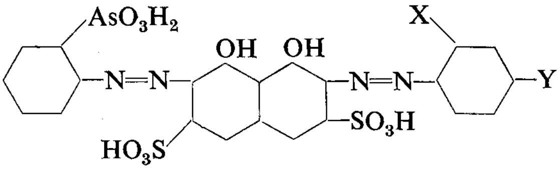
Arsenazo III can also be used for the photometric determination of zirconium and hafnium when both elements are present. The principle of the method has been described earlier and is general for all reagents giving colour reactions with zirconium and hafnium. It is as follows: the sum of zirconium + hafnium is determined photometrically at two pH values at which superposition is observed in the first case and at which, in the second case, the largest discrepancy occurs between the colour intensity of the corresponding zirconium and hafnium complexes.[14] The zirconium and hafnium contents can be calculated from the results obtained.[14] Elinson and Mirzoyan state that the photometric determination of zirconium + hafnium should be carried out in 1*N* and 4*N* hydrochloric acid.

Rare earths

In weakly acidic solutions yttrium, lanthanum and the lanthanides develop a blue-green coloration with arsenazo III. Scandium gives a violet colour. The determination is of a sufficiently high degree of sensitivity: 0.5 μg of the element and larger quantities can be determined in 25 ml of solution. The reaction is not very selective: all elements reacting with arsenazo III act as inhibitors when the pH at which they begin to hydrolyse is lower than the pH of the start of the hydrolysis of the rare earth elements. The following substances do not act as inhibitors in quantities up to 5–50 mg in 25 ml: aluminium, iron, magnesium, sodium, potassium, sulphates, chlorides, phosphates.[15]

Analogues of arsenazo III

Kuznetsov, Dedkov and Savvin[6] succeeded in synthesising completely different analogues of arsenazo III by the azo-addition of arsenazo I and various amines on adding calcium salts:



where $X = H$; $Y = H_3SO_3H$, NH_2 NO_2, $N(CH_3)_2$, AsO_3H_2;
$Y = H$; $X = COOH$, SO_3H, OH, NO_2.

Preliminary analytical tests have proved that these compounds also give colour reactions with many elements, especially with those where arsenazo I and arsenazo III give colour reactions. The stability of complexes formed by these compounds lies between the stability of the corresponding complexes of arsenazo I and arsenazo III. Further investigations will be carried out on the bis-azo-derivatives of chromotropic acid.

Synthesis of arsenazo III

The synthesis is quite simple and easily reproducible.

The compound is prepared by the azo-addition of concentrated solutions of diazotised *o*-aminophenylarsonic acid and chromotropic acid in a medium of excess calcium hydroxide which is used simultaneously as a base and as an activator.[3]

Dissolve 15 g (0·069 mole) of *o*-aminophenylarsonic acid, whilst heating slightly, in 30 ml of water and 15 ml of conc. hydrochloric acid (sp. gr. 1·18). After cooling, add 50 g of crushed ice. To this mixture add, with constant stirring, a solution of 5 g of sodium nitrite in 10–15 ml of water and a small excess of nitric acid (accurately tested with iodised starch paper) which is subsequently removed with sulphamic acid.

Dissolve 6·5 g (0·0179 mole) of the disodium salt of chromotropic acid in 20 ml of water and introduce a mixture of 10 g of calcium oxide and 30 ml of water into the solution. Add 50 g of crushed ice as well as the previously prepared diazonium solution, under constant agitation. The solution turns a blue–violet colour. Allow to stand for 30 min to 2 hr at room temperature.

Carry out tests to ascertain the termination of the azo-addition reaction. Add 1 drop of the reaction mixture (*ca.* 0·03 ml) to 50–100 ml of water. Place 5–10 ml of the resulting blue solution in a test tube and to this add 2–3 drops of conc. hydrochloric acid. The solution turns pinkish-crimson. Add 1 drop of thorium salt solution, containing 10–20 mg/ml of thorium, when the solution acquires the intensive emerald-green colour of the thorium-arsenazo III complex. Decant the solution into two test tubes and to one test tube add 10–15 drops (*ca.* 0·5 ml) of conc. sulphuric acid, whilst constantly agitating and cooling the contents of the test tube. The colour of the solution to which conc. sulphuric acid has been added will differ slightly from the colour of the second fraction if complete addition has occurred; it will turn dark green. If, on the other hand, incomplete addition took place, then the fraction containing sulphuric acid will turn red-violet, crimson or acquire a muddy colour; in this case a mixture of arsenazo I and arsenazo III has been obtained. This may be caused by inadequate purity of the starting materials, *i.e.* of the chromotropic acid and especially of *o*-aminophenylarsonic acid.

Add 1 litre of hot water and 100 ml of conc. hydrochloric acid to the mixture obtained by the addition reaction. Agitate the mixture to dissolve the calcium salts completely, and filter after allowing to settle. Wash the almost black residue with 50–100 ml of hydrochloric acid (1:10) and discard the filtrate. Dissolve the crude product in 1 litre of hot water + 50 ml of 40% sodium hydroxide solution, freed from mechanical admixtures by filtration, acidify with 100 ml of conc. hydrochloric acid and allow to stand for a few hr or overnight. Filter off the precipitate, centrifuge and wash it first with 30–50 ml of water, then with 30–50 ml of ethanol. The last fractions of the filtrate should be free from reaction by-products, *i.e.* from arsenazo I and decomposition products of the excess diazonium compound of *o*-aminophenylarsonic acid. This is tested by the above described qualitative reaction with thorium salts. The yield of arsenazo III is 11–12 g.

Zusammenfassung—Das Reagens Arsenazo III (1,8-dioxynaphthalin-3,6-disulfonsäure-2,7-bis [azo-2-phenylarsinsäure]) gibt Farbreaktionen mit einer Reihe von Elementen. Anionen beeinflussen die Färbungen nur zu einem geringen Grade und es ist möglich bei niederen pH-Werten zu arbeiten. Die Reaktion ist sehr sensitiv und kann zur photmetrischen Bestimmung von Th, Zr, Hf, U und einiger, anderer Metalle herangezogen werden. Th, Zr und U zeigen die höchste Empfindlichkeit. Material, welches diese Elemente enthält, kann direkt nach Auflösen der Probe und ohne weitere Abtrennungen zur Analyse herangezogen werden.

Résumé—Le réactif arsénazo III (1,8-dihydroxynaphtalène-3,6-disulfonique acide-2,7-bis[azo-2-phénylarsonique acide]) donne des réactions colorées avec un certain nombre d'éléments. Les anions n'influent que très peu sur les réactions, et il est possible de travailler à de faibles valeurs de pH. La réaction est très sensible, le composé peut ensuite être utilisé pour le dosage photométrique de Th, Zr, Hf, U et d'autres éléments. La méthode est la plus sélective pour Th, Zr et U(IV). Les matériaux contenant ces éléments peuvent être analysés directement, dans des solutions formées après dissolution des échantillons, sans séparation des éléments.

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Talanta, 1961, Vol. 8, pp. 686 to 688. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATION

Chelatometric determination of caesium

(*Received* 5 *May* 1961. *Accepted* 15 *May* 1961)

INTRODUCTION

CAESIUM salts must be carefully dried and dehydrated before being weighed. These operations require special care and several hours may elapse before constant weight is attained. On the other hand, caesium salts, being much more volatile than the corresponding sodium salts, may suffer a partial volatilisation through rapid or prolonged heating, especially when minute quantities of caesium perchlorate are treated.

These difficulties suggested to the author the advisability of using a titrimetric procedure for the determination of caesium, utilising the perchlorate precipitate obtained by the classical technique. The literature on chelatometric titrations does not mention any method, direct or indirect, for the determination of caesium.

The principle of the present method is based on the transformation of the perchlorate to caesium chloride[1,2] followed by precipitation of the chloride with silver nitrate. The chelatometric procedure for the titration of silver[3,4] is applied. This is based on the nickel that is liberated when the silver salt is treated with potassium nickelicyanide:

$$2AgCl + [Ni(CN)_4]^{2-} \rightarrow 2[Ag(CN)_2]^- + Ni^{2+} + 2Cl^-$$

The liberated nickel is titrated with EDTA, using murexide to indicate the end-point.

EXPERIMENTAL

Reagents

Ammonium chloride: AnalaR.

Silver nitrate: 5% and 0·1% aqueous solutions.

Nitric acid: Concentrated, and 1% aqueous.

EDTA: 0·1*M* (or, if necessary, 0·01*M*).

Murexide: Saturated aqueous solution.

Potassium nickelicyanide: 0·1*M*. Titrate 0·1 mole of $NiSO_4$ in 500 ml of water, made ammoniacal, with 1*M* KCN until murexide changes from yellow to purple. Dilute the solution to 1 litre.

Procedure

The caesium perchlorate precipitate is dried rapidly by washing it with a little ether, and it is then removed carefully from the Gooch filter* and introduced into a platinum dish. Two to three g of ammonium chloride are added and mixed intimately with the precipitate. The mixture is covered with a layer of ammonium chloride and heated gently for 1–2 hr, the dish being covered with a watch glass. If a porcelain dish is used, 1 ml of chloroplatinic acid is added to catalyse the reaction.

The temperature should be kept below the melting point of the residual chloride (otherwise the platinum dish may be damaged). More ammonium chloride is added and the mixture is heated for another 0·5 hr. The contents of the dish are cooled and then dissolved in water in a beaker. A few drops of concentrated nitric acid are added and afterwards an excess of 5% silver nitrate solution. The contents of the beaker are boiled for 5 min, the beaker being covered with a watch glass.

When cold, the contents of the beaker are filtered through a Gooch filter. The precipitate is washed twice with 0·1% silver nitrate solution and then twice with 1% nitric acid. The filter and precipitate are introduced into a beaker containing ammoniacal potassium nickel tetracyanide

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* If a very small quantity of caesium is analysed, the $CsClO_4$ precipitation is better carried out in a centrifuge tube.

solution. The beaker is warmed gently until dissolution of the precipitate is complete. A few drops of murexide solution are added and the solution is titrated with 0·1*M* EDTA to a yellow to purple end-point.

$$0{\cdot}1M \text{ EDTA solution, } ml \times 26{\cdot}582 \equiv \text{Cs}, mg$$
$$0{\cdot}1M \text{ EDTA solution, } ml \times 28{\cdot}182 \equiv \text{Cs}_2\text{O}, mg$$

RESULTS AND DISCUSSION

The results obtained by the above method are very satisfactory. Some results with a solution of caesium carbonate are reproduced in Table I. The analytical reagent was dried at 110° for 4 hr and 5·7805 g were dissolved in 1000 ml of twice distilled water. One ml of this solution is equivalent to 5 mg of Cs_2O. The caesium carbonate was transformed into caesium perchlorate and was then treated by the method described. Titrations 1–5 were carried out with 0·01*M* EDTA and titrations 6–10 with 0·1*M* EDTA.

TABLE I.

No.	Cs_2O taken, *mg*	Cs_2O found, *mg*	Difference, *mg*	Difference, %
1	5·0	5·1	+0·1	+2·0
2	10·0	9·9	−0·1	−1·0
3	15·0	15·1	+0·1	+0·7
4	20·0	19·8	−0·2	−1·0
5	30·0	30·1	+0·1	+0·3
6	40·0	40·2	+0·2	+0·5
7	50·0	50·3	+0·3	+0·6
8	75·0	74·7	−0·3	−0·4
9	100·0	100·5	+0·5	+0·5
10	200·0	201·6	+1·6	+0·8

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Summary—An indirect chelatometric method for the determination of caesium is described. Caesium is precipitated as perchlorate according to the classical procedure and the precipitate is heated with ammonium chloride to reduce the perchlorate to chloride. Caesium chloride is dissolved in water and the chloride is precipitated as silver chloride. This precipitate is dissolved in an ammoniacal solution of potassium nickelicyanide. Silver displaces nickel in the complex and the freed nickel is titrated with EDTA. Caesium is obtained indirectly by multiplying the quantity of EDTA solution by a factor. The results are very satisfactory and the method is as rapid as the gravimetric procedure, with the advantage of avoiding the tedious drying and weighing of the perchlorate precipitate.

Zusammenfassung—Eine indirekte, chelatometrische Methode zur Bestimmung von Cäsium wird beschrieben. Cäsium wird als Perchlorat gefällt und durch Erhitzen des Niederschlages mit Ammoniumchloride zu Cäsiumchlorid reduziert. Letzteres wird in Wasser gelöst, Chlorid mit Silber gefällt und das Silberchlorid mit Nickeltetracyanid umgesetzt. Das in Freiheit gesetzte Nickelwird chelometrisch bestimmt. Die Methode gibt sehr gute Resultate und vermeidet das zeitraubende Trocknen und Wägen des Niederschlages.

Résumé—L'auteur décrit une méthode complexométrique indirecte de dosage du caesium. Le caesium est précipité sous forme de perchlorate suivant le procédé classique; le précipité est chauffé avec du chlorure d'ammonium pour réduire le perchlorate en chlorure. Le chlorure de caesium est dissous dans l'eau, et le chlorure est précipité à l'état de chlorure d'argent. Ce précipité est dissous dans une solution ammoniacale de nickelocyanure de potassium. L'argent déplace le nickel de son

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complexe, et le nickel libre est titré par complexométrie. La quantité de caesium est obtenue indirectement en multipliant la quantité de solution d'EDTA utilisée par un facteur. Les résultats sont très satisfaisants, et la méthode est aussi rapide que la gravimétrie, elle a de plus l'avantage d'éviter le séchage pénible et la pesée du précipité de perchlorate.

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Talanta, 1961, Vol. 8, pp. 689 to 691. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

Material for this section should be sent directly to the Assistant Editor

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DEUTSCHLAND

Dienstag–Freitag 10–13 *April* 1962: **Erstes Europäisches Symposium "Zerkleinern"**, 36. Veranstaltung der Europäischen Föderation für Chemie-Ingenieur-Wesen: vorbereitet und durchgeführt von *der Verfahrentechnischen Gesellschaft (VTG) im Verein Deutscher Ingenieure* und *der DECHEMA Deutsche Gesellschaft für chemisches Apparatewesen, Frankfurt (Main).* Frankfurt (Main), Deutschland.

Drei Themengruppen werden behandelt, und zwar: Gruppe (A) Physikalische und theoretische Grundlagen des Zerkleinerns Gruppe (B) Grundlagen und neuere Entwicklungen der Zerkleinerungs maschinen

Gruppe (C) Anwendungstechnik, Zerkleinerung bestimmter Stoffe.

Sekretariat: Verfahrenstechnische Gesellschaft
Frankfurt (Main) 7, Rheingau-Allee 25.

FRANCE

Lundi–Mardi 9–10 *Octobre* 1961: **Commission Internationale d' Analyses;** *Comite International de la Detergence. Paris.*

ITALY

Thursday–Friday 9–10 *November* 1961: **Scientific and Technical Documentation and Information in Chemistry:** Under the auspices of *I.U.P.A.C.* and *Federation of Scientific and Technical Associations of Milan* and organised by *Lombard Section of Italian Chemical Society, Italian Society of Pharmaceutical Sciences* and *Italian Association of Chemical Engineering* with co-operation of *Centre Français d'Exchanges et de Documenation Technique.* House of the Scientific and Technical Associations, 10, Via del Politechnico, Milan.

The programme has been provisionally arranged to cover:

1. Publication of documents.
2. Organisms of documentation and information.
3. Current and retrospective bibliographies.
4. Automation in the research for information.

POLAND

Thursday–Friday 28–29 *September* 1961: **Symposium on Gas Chromatography:** *Section of Gas Analysis of Analytical Committee of Polish Academy of Sciences* and the *Chief Technical Organisation.* Kraków.

The programme will include a number of general lectures and scientific communications given by Polish, Czechoslovakian and German Democratic Republic participants. Some lectures by manufacturers of apparatus (Pye, Siemens) are also expected.

SWITZERLAND

September 1963: **Second Congress of International Federation of Automatic Control:** On the invitation of *Swiss Association for Automatic Control.* Basle.

Nearly all papers should deal with theory or with applications of automatic control. A few papers will be adopted on components of control devices and on general items. Papers should deal with one of the following problems:

1. Theory
    - (a) Discrete Systems
    - (b) Stochastic Systems
    - (c) Optimal Systems
    - (d) Learning Systems
    - (e) Systems Reliabilty

2. Applications
    - (a) Process Dynamics
    - (b) Computer Studies of Applications, on or off line
    - (c) Optimising or Adaptive Control Applications

3. Components
    - (a) New and Effective Devices
    - (b) Measurement of the Reliability of Components

Papers may be submitted in English, French, German or Russian.

Enquiries should be addressed to Secretary of I.F.A.C., Dr.-Ing. G. RUPPEL, Prinz-Georg-Strasse 79, Düsseldorf, Germany.

UNITED KINGDOM

National Lending Library for Science and Technology of D.S.I.R. has recently published a list of Irregular Serials received from U.S.S.R. and Bulgaria. The main part of the list is arranged in alphabetical order of the title using the cyrillic alphabet. Following the main list, there is a short list of serials received from Latvia, Lithuania and Estonia and published in the roman alphabet, A list of books received from U.S.S.R. has also recently been established.

Listed items may be borrowed from National Lending Library of D.S.I.R., Boston Spa, Yorkshire.

Tuesday–Friday 18–21 *September* 1962: **First International Congress of Food Science and Technology.** Imperial College of Science and Technology, London.

The programme is divided into four sections, which will run concurrently throughout the four days of the Congress except for a number of periods devoted to Plenary Sessions and Congress Symposia:

Section A. Chemical and Physical Aspects of Foods.

Section B. Biological and Microbiological Aspects of Foods.

Section C. Quality, Analysis and Composition of Foods.

Section D. Manufacture and Distribution of Foods.

The following sub-sections are envisaged to Section C:

1. Specialised analytical techniques.
2. Detection and determination of minor constituents.
3. Application of automation to analysis and quality control.

Further details and registration forms may be obtained from Mr. F. J. GRIFFEN, 14, Belgrave Square, London, S.W.I.

UNITED STATES OF AMERICA

Sunday–Thursday 1–5 *October* 1961: **Fall Meeting:** *Electrochemical Society.* Statler Hilton Hotel, Detroit, Mich.

Monday–Thursday 9–12 *October* 1961: **Eleventh Annual Instrument Symposium and Research Equipment Exhibit:** *Washington Sections of American Chemical Society, Instrument Society of America, American Association of Clinical Chemists, Society of American Bacteriologists, Society for Applied Spectroscopy* and *Society for Experimental Biology and Medicine.* National Institutes of Health, Bethesda, Md.

Monday–Wednesday 16–18 *October* 1961: **Ninth Detroit Anachem Conference:** *Association of Analytical Chemists.* Wayne State University.

Monday–Thursday 16–19 *October* 1961: **Second International Vacuum Congress:** *International Organisation for Vacuum Science and Technology* and *American Vacuum Society.* Sheraton Park Hotel, Washington, D.C.

Friday 20 *October* 1961: **Fifth Annual Symposium on Advances in Tracer Methodology:** *New England Nuclear Corporation.* Shoreham Hotel, Washington, D.C.

Wednesday–Friday 15–17 *November* 1961: **1961 Eastern Analytical Symposium and Instrument Exhibit:** *Analytical Groups of New York and North Jersey Sections of American Chemical Society, New York, Delaware Valley, New England and Baltimore-Washington Sections of Society for Applied Spectroscopy* and *Metropolitan Microchemical Society.* Statler Hilton Hotel, New York City.

The meeting will consist of a series of 3-hour symposia of invited papers of extended length by experts in a number of fields of interest to analysts. The emphasis will be on recent developments in these specialities.

The programme headings are as follows:

Wednesday 15 *November*

Detectors for Gas Analysis.
X-Ray Spectroscopy.
Storage and Retrieval of Infrared Spectral Data.

Gas Chromatography with High Molecular Weight Organic compounds.
Nuclear Magnetic Resonance.
Emission Spectroscopy.

Thursday 16 *November*

Mass Spectroscopy.
Electroanalytical Methods.
Automation in Microchemical Analysis—Panel Discussion.
Advances in Instrumentation: Infrared Spectroscopy Clinic.

Advances in Biochemical Analysis.
Electroanalytical Methods.
New Developments in Instrumental Techniques for Molecular Weight Determinations.
Advances in Instrumentation:
(a) Emission Spectroscopy Clinic
(b) X-Ray Spectroscopy Clinic.

Friday 17 *November*

Food Additive Analysis.
Applications of Radioistopes.
Advances in Physical and Chemical Separations.

Applications of Nuclear Activation Analysis.
Advances in Physical and Chemical Separations.

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PAPERS RECEIVED

A spot test for uranium^{VI} with resacetophenone-oxime: C. Rama Rao. (6 *June* 1961).

Spectrophotometric studies on technetium and rhenium: M. Al-Kayssi, R. J. Magee and C. L. Wilson. (27 *June* 1961).

New redox systems-IV: Oxidation of cobalt^{II} with iron^{III} salts in 2:2 bipyridyl solutions. Frantisek Vydra and Rudolf Přibil. (27 *June* 1961).

A pH-metric study of some bivalent metal sulphosalicylates: V. S. K. Nair. (29 *June* 1961).

The photometric determination of scandium by means of α-(2, 4-dioxyphenylazo)-pyridine: A. I. Busev. (3 *July* 1961).

Contribution to the basic problems of complexometry-IX: Thioglycollic acid as masking agent Rudolf Přibil and Vladimir Vesely. (3 *July* 1961).

A qualitative test for detection of ferrocenes: J. D. Behun. (10 *July* 1961).

A comparative study of some lanthanon chelates of alizarin complexan as reagents for fluoride: R. Belcher and T. S. West. (10 *July* 1961).

A study of the cerium^{III} alizarin complexan-fluoride reaction: R. Belcher and T. S. West. (10 *July* 1961).

Thermogravimetric analysis of potassium hydrogen phthalate: A. E. Newkirk and Renette Laware. (17 *July* 1961).

Radiochemical separation of indium by amalgam exchange: R. R. Ruch, J. R. Devoe and W. W. Meinke. (18 *July* 1961).

Infrared correlations in the bile acid series: Samuel J. Levin and Charles G. Johnston. (17 *July* 1961).

Steric effect of ortho-substituted alkyl groups on chromatographic absorption of aniline: Jack K. Carlton and Floyd B. O'Neal. (17 *July* 1961).

Activation analysis of molybdenun in plant material: B. Van Zanten, D. Decat and G. Leliaert. (19 *July* 1961).

A scheme for the rapid analysis of uranium-ore acid leach solutions: Lyn Jarman and M. Matic. (20 *July* 1961).

Potentiometric acid-base titration in acetone-water solutions of nitrocellulose: L. R. Leake and G. F. Reynolds. (1 *August* 1961).

Photometric titrations-V: A selective chelometric determination of cobalt: H. Flaschka and J. Ganchoff. (1 *August* 1961).

Emission spectra from high-frequency excitation-II: The spectra of nitrogen, hydrogen, ammonia: C. L. Chakribarti, R. J. Magee and C. L. Wilson. (1 *August* 1961).

Talanta, 1961, Vol. 8, pp. 693 to 694. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

The solubility of bis-8-quinolinolo-zinc*

SIR:

As part of an investigation of factors influencing the intrinsic solubility of chelates, the solubility of several metal 8-quinolinolates have been studied. At this time we would like to communicate the results of our study of the solubility of bis-8-quinolinolo-zinc at 25° and an ionic strength 0·1 molar. The results provide evidence for the existence of $Zn(Ox)_3^-$, a species not considered in previous studies.[1]

In order to minimise the importance of reactions of zinc with other bases, the solubility measurements were made in 8-quinolinol solutions in the absence of foreign buffers in the interval pH 3·1 to 4·1. Over the range pH 3·9 to 9·9, the solutions were saturated with respect to 8-quinolinol, with buffers present in several instances. In this way, the conditions under which the solubility of bis-8-quinolinolo-zinc was determined were different from those reported recently.[1]

The chelate was prepared from an acetic acid solution of ^{65}Zn and zinc perchlorate in the manner described[2] to yield crystals whose powder pattern was identical with that of powdered single dihydrate crystals of bis-8-quinolinolo-zinc. Samples of solution were removed from a solubility apparatus which contained a stirred solvent chelate mixture at 24-hr intervals until equilibrium was attained. The results appear in Table I.

TABLE I.—SOLUBILITY OF BIS-8-QUINOLINOLO-ZINC

pH	pOx	pS
3·12	10·41	2·69
3·16	10·24	2·98
3·40	9·79	3·74
3·59	9·56	4·16
3·74	9·22	4·63
3·90	8·91	5·25
4·14	8·40	6·01
†3·94	8·08	6·56
†4·59	7·43	7·24
†5·62	6·40	7·45
†6·82	5·20	7·46
†7·12	4·90	7·21
†8·73	3·30	6·41
†9·39	2·66	5·62
†9·94	2·14	5·35

† Saturated with 8-quinolinol.

From values reported for the acid dissociation constants[3,4] and intrinsic solubility[3] of 8-quinolinol under the same conditions of temperature and ionic strength, the concentration of the 8-quinolinol anion, $[Ox^-]$, may readily be calculated for each hydrogen ion concentration which prevailed in solution. The values were plotted as the negative logarithm of the 8-quinolinol anion concentration, pOx, against the negative logarithm of the zinc solubility, pS. Proceeding from the lowest 8-quinolinol anion concentration, the solubility of zinc appeared to decrease continuously, pass through a minimum, and increase continuously.

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* Presented in part to the 138th meeting of the American Chemical Society in New York, N. Y., September 11 to 16, 1960.

The values were treated according to the graphical methods described by Sillén.[5] On the acid side of the solubility minimum, the experimental points were compared to normalised curves of the type

$$f(a) = c_0 + c_1a + c_2a^2$$

and on the basic side to

$$f(a) = c_0 + c_3/a$$

where

$$f(a) = S, \quad c_0 = \beta_2 K_{S0}, \quad c_1 = k_1 K_{S0}, \quad c_2 = K_{S0}, \quad c_3 = \beta_3 K_{S0},$$

and

$$a = 1/[\mathrm{Ox}^-].$$

This procedure will be most successful for the case, $k_3 \ll k_2$.

The values obtained were $\log K_{S0} = -23{\cdot}34$, $\log k_1 = 8{\cdot}52$, $\log k_2 = 7{\cdot}32$, $\log k_3 = 4{\cdot}32$. These constants may be compared with values of the solubility product, $\log K_{S0} = -23{\cdot}73$, and the first formation constant, $\log k_1 = 8{\cdot}12$, reported previously for an ionic strength of 0·1 *M* and 20°.[6] Although k_3 corresponds to the formation of the species $\mathrm{Zn(Ox)_3}^-$, the solubility measurements do not preclude the formation of species of the type $\mathrm{Zn(Ox_2OH)}^-$ in the region of increasing zinc solubility. In this connection, it is of interest to note that the stabilities of chelates with 8-quinolinol and 8-quinolinol-5-sulphonic acid are nearly the same.[7] Potentiometric measurements[8,9] have indicated that nickel$^{\mathrm{II}}$, for example, exhibited its maximum co-ordination number toward 8-quinolinol-5-sulphonic acid and 2-methyl-8-quinolinol-5-sulphonic acid. However, reliable measurements could not be made in the region in which the addition of a third 5-sulphonic acid derivative to zinc would occur as predicted from the solubility measurements.

The peculiarly large solubilities observed by Merritt and Weber probably reflect the formation of zinc species that would occur in the absence of a sufficient excess of reagent. Early in our investigation we encountered similar difficulties. A more detailed report will be published later.

Acknowledgment—The authors gratefully acknowledge the financial assistance of the U.S. Atomic Energy Commission in this work.

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Department of Chemistry
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Tucson 25, *Arizona, U.S.A*
11 *May* 1961

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Talanta, 1961, Vol. 8, pp. 695 to 696. Pergamon Press Ltd. Printed in Northern Ireland

LATE NOTICES

JAPAN

Monday–Saturday 25–30 *September* 1961: **International Conference on Magnetism and Crystallography including Symposium on Electron and Neutron Diffraction:** *International Union of Pure and Applied Chemistry and International Union of Crystallography.* Kyoto, Japan.

UNITED KINGDOM

Thursday–Friday 5–6 *October* 1961: A series of papers on **Selected Topics originating from Analytical Requirements in the Field of Nuclear Technology:** *Society for Analytical Chemistry.* Institution of Mechanical Engineers, Birdcage Walk, London, S.W.1.

Tuesday 10 *October* 1961: **Research Work in Analytical Chemistry at the Technical University of Budapest:** Professor L. ERDEY: *Society for Analytical Chemistry, Midlands Section* and *Royal Institute of Chemistry, Birmingham and Midlands Section:* Joint Meeting. University, Edgbaston, Birmingham, 15. 7.00 p.m.

Wednesday 25 *October* 1961: **Some Special Problems in the Polarography of Indium and Tellurium:** Professor Dr. M. VON STACKELBERG: *Polarographic Society.* School of Pharmacy, 29–39, Brunswick Square, London, W.C.1. 2.45 p.m.

Thursday 26th *October* 1961: **Aquametry:** Dr. J. H. THOMPSON: *Society for Analytical Chemistry, Midlands Section.* Technical College, Nottingham, 7.00 p.m.

Wednesday–Saturday 28–31 *March* 1962: **Third Symposium on Spectroscopy:** *Institute of Petroleum, Hydrocarbon Research Group.* William Beveridge Hall, University of London.

The symposium will be similar to those held in 1954 and 1958 and will review progress in many spectroscopic fields. These will include:

Infrared and Raman spectroscopy,
Nuclear and electron-spin resonance,
Vacuum ultraviolet spectra and ionisation potentials,
and X-ray fluorescence and atomic absorption spectra.

Applications for attendance and further details should be sent to The General Secretary, Institute of Petroleum, 61, New Cavendish Street, London, W.1.

Thursday–Friday 27–28 *September* 1962: **Symposium on Techniques of Polymer Science:** *Society for Chemical Industry, Plastics and Polymer Group.*

Papers concerned with novel techniques in polymer synthesis, analysis, including structural analysis, and measurement of physical properties will be featured.

Summaries of proposed contributions should be sent to the Convener of Symposium Sub-committee, 14, Belgrave Square, London, S.W.1, before 1st December, 1961. Complete typescripts of papers provisionally accepted will be called for by 1st June, 1962.

Bureau of Analysed Samples Ltd. has issued the following new British Chemical and Spectrographic Standard Samples:

B.C.S. 300: 6% zinc-aluminium alloy, analysed for Cu, Mn, Si, Mg, Fe, Ti, Cr and Zn.
B.C.S. 304: 10% aluminium bronze, analysed for Cu, Zn, Ni, Fe, Mn, Si and Al.
B.C.S. 305: 75% ferro-silicon, analysed for P. Al, Ca and Si.
B.C.S. 306: 0.4% carbon free-cutting steel, analysed for Si, S, P, Mn and C.

These samples are only available in the finely divided form for chemical analysis.

S.S. 21-24: a series of low tungsten steels analysed for tungsten only, with tungsten contents ranging from 0.7–3.4%.

This series is supplied in the form of 0.75–in. diam. rods, each 3 in. long, for use as spectrographic standards, but is also available in the form of turnings for chemical analysis bearing the reference numbers B.C.S. 281–284.

Further details of these new samples are given in List No. 400R and the latest supplementary insert sheet, which is obtainable free on request from Bureau of Analysed Standards Ltd., Newham Hall, Middlesbrough.

The first of the Society for Analytical Chemistry's Monographs, **Methods for the Analysis of non-soapy Detergent (NSD) Products,** by G. F. LONGMAN and J. HILTON, has recently been published. The Monograph, bound in stout paper covers, uniform in size with *The Analyst*, contains in 30 pages a complete practical scheme for the determination of all components of most non-soapy detergents at present marketed. It is available only from the Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1, (*not* through booksellers) at 15s. ($2.00), post free.

A booklet on **Quality Measurement in the Chemical Industry** has recently been published by D.S.I.R.

A physicist and a physical chemist discuss the use of instruments to control processes in the production of chemicals. The authors conclude that all plants should have skilled analysts for measuring product quality, but where successful functioning of a process depends on a large number of routine analytical operations it is worthwhile to consider whether an instrument would be a more effective way of doing the job.

Copies are obtainable free from D.S.I.R. Library, Charles House, 5–11 Regent Street, London, S.W.1.

B.S.I. News announces the following new British Standard: *B.S.* 3397: 1961; *Methods of testing synthetic rubber latices.* This covers method of sampling, and methods for the determination of total solids, coagulum, pH and surface tension. (Price 4s.)

The following revised British standards are also announced:

B.S. 1377: 1961: *Methods of testing soils for civil engineering purposes.* (Price 30s.)

The contents are divided into:

Part 1. General (glossary and list of symbols, apparatus, soil grouping, preparation of samples).
Part 2. Soil classification tests.
Part 3. Soil chemical tests.
Part 4. Soil compaction tests.

B.S. 1747: *Methods for the measurement of air pollution: Part* 1: 1961: *Deposit gauges.* This covers the construction, installation and use of the deposit gauge for the collection and measurement of atmospheric pollution impurities that are deposited by their own weight or with the assistance of rain. The gauge also provides an estimate of the rainfall. A standard report form and a statement of the analytical determinations to be made are included. (Price 5s.)

UNITED STATES OF AMERICA

Thursday–Saturday 28–30 *September* 1961: **Fifth Annual Conference:** *Chemical Division of American Society for Quality Control.* Daniel Boone Hotel, Charleston, W. Va.

Tuesday–Thursday 10–12 *October* 1961: **Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology and Second Conference on Nuclear Chemistry:** *Reactor and Analytical Chemistry Divisions, Oak Ridge National Laboratory.* Civic Auditorium, Gatlinburg, Tennessee. (See also *Talanta*, 1961, **8**, 451).

The programme for the Analytical Chemistry Conference has been arranged under the following headings:

Tuesday 10 *October*
Morning session—Instrumentation
Afternoon session—Spectral Methods of Analysis
Wednesday 11 *October*
Morning session—Burnup and Radiochemical Analysis
Afternoon session—Radiochemical and Activation Analysis
Thursday 12 *October*
Morning session—Analysis of Reactor Materials
Afternoon session—Analysis of Reactor Materials

It is anticipated that the proceedings of the two conferences will be published by the U.S. Atomic Energy Commission.

Enquires concerning the meeting in general and communications relative to the Analytical Chemistry Conference should be addressed to: C. D. SUSANO, Oak Ridge National Laboratory, P.O Box X, Oak Ridge, Tennessee.

NOTES FOR CONTRIBUTORS

1. General

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

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, but should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

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

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

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

2. Script Requirements

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

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

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

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

5. Illustrations should be separate from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require re-drawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, since they are easily available to the printers:

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

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

8. **References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:**

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

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

9. Except in the case of preliminary communications, proofs will be sent out to authors for correction. For papers these will be in page form. **It is emphasised that at this stage extensive alterations to the text or failure to return the corrected proofs promptly may result in serious delay in publication.**

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

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

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

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Short communication

Letter to the Editor

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