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1) *Chem. Eng. News*, 1960, **38** **(16)**, 115.
2) Callear, A. B. and Cvetanovic, R. J., *Canad. J. Chem.*, 1955, **33**, 1256-67.
3) Hishta, C., *et al.*, *Anal. Chem.*, 1960, **32** (7), 880.

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1) Pollard, F. H., Hanson, P. and Geary, W. J., *Anal. Chim. Acta*, 1959, **20**, 26-31.
2) Wehber, P.. *Z. anal. Chem.*, 1959, **166**, 186-9.
3) Busev, A. I. and Kanaev, N. A., *C.A.*, 1959, **53**, 18747c.

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1) Billman, J. H., Janetos, N. S., and Chernin, R., *Anal. Chem.*, 1960, **32**, 1342-4.

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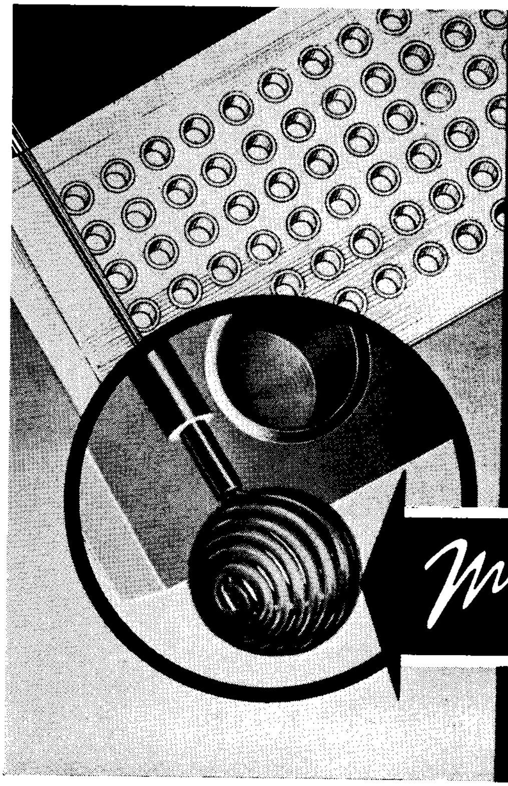

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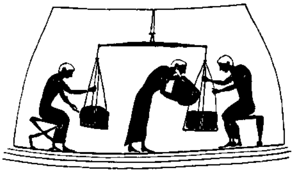

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* 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.

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Talanta, 1962, Vol. 9, pp. 341 to 348. Pergamon Press Ltd. Printed in Northern Ireland

DIE BESTIMMUNG KLEINER FLUORMENGEN—II

DIE BESTIMMUNG VON FLUOR MIT ZR-ERIOCHROMCYANIN-LACK OHNE VORHERIGE ABTRENNUNG IN STARK MINERALISIERTEN WÄSSERN

Roman Valach
Geologische Zentralanstalt, Prag, Tschechoslowakei

(*Received* 5 *September* 1961. *Accepted* 20 *November* 1961)

Zusammenfassung—Es wird eine hochempfindliche spektrophotometrische und photometrische Bestimmung von Fluor beschrieben, welche auf der Entfärbung des Zirkonium-Erichromcyanin-Lackes in 0,2 n Salzsäure beruht. Der Störeffekt eines großen Sulfatüberschusses wird auch bei hohen Bikarbonat- oder Kieselsäure-Gehalten durch Fällung von Bariumsulfat aus der schwachsaueren Lösung von sehr niedriger Fluorkonzentration ausgeschaltet, wo die Mitfällung von Bariumfluorid nicht eintritt. Das Fluoaluminat wird durch Alkalisieren zerlegt. Die Bildung einer störenden Eisen(III)-Eriochromcyanin-Verbindung wird durch Abwarten der Abscheidung von Eisenhydroxyd nach Entweichen des Kohlendioxyds verhindert.

Aus der kritischen Übersicht der Bestimmungen von Fluor[1] folgt, daß die Bestimmung von kleinen Fluor-Totalkonzentrationen nach der meistens zeitraubenden Abtrennung von ihrer Begleitkomponenten nur selten prinzipielle Vorteile hat. Der Autor widmete deshalb der Zr-Eriochromcyanin-Methode seine Aufmerksamkeit, da sich bei ihr nach Literaturangaben Störungen durch anwesende Kationen und Anionen am wenigsten bemerkbar machen und modifizierte sie so, daß auch bei Analysen von stark mineralisierten Wässern keine besondere Fluor-Abtrennung vorausgehen muß.

Nach experimentell nicht bewiesenen Angaben[3,4] kann man Sulfate, welche bei Fluor-Analysen von höher mineralisierten Wässern meistens die größten Fehler verursachen, als Bariumsulfat abtrennen, obwohl derselbe Niederschlag auch als Kollektor des wenig löslichen Bariumfluorids dient.[5] In der vorliegenden Arbeit wird deshalb vor allem die Beseitigung der durch Sulfate bewirkten Störung beschrieben.

EXPERIMENTELLER TEIL

Die Messungen wurden mit Hilfe des Spektrophotometers Uvispek der Firma Hilger mit Wolfram-Glühbirne und Glasprisma (Spaltbreite 0,1 mm) und mit Hilfe des Photometers Spekker derselben Firma (Filter 520 und 550 mμ) in Glasküvetten mit 4 cm Meßlänge (wenn nichts anderes angeführt ist) durchgeführt.

Die Stammlösung von 0,100 mg F^-/ml wurde durch Auflösen von 0,2210 g Natriumfluorid (p.a. Merck) in 1000 ml dest. Wasser zubereitet und in einer paraffinierten Flasche aufbewahrt. Durch Verdünnen der Stammlösung im Verhältnis 1 + 19 wurde die Eichlösung von 5 μg F^-/ml hergestellt.

Die Eriochromcyanin-Lösung (im weiteren Text verkürzt ECC) wurde durch Auflösen von 1,20 g ECC (Merck) in 1000 ml dest. Wasser zubereitet. Zur Stabilisierung wurde mit 1 ml konz. chlorfreier Salzsäure angesäuert, und zum Schutz vor Verschimmelung wurde Quecksilberjodid bis zur Sättigung zugegeben.

Die Zirkonium-Lösung wurde durch Auflösen von 0,160 g $ZrOCl_2 \cdot 8H_2O$ in ungefähr 40 ml dest. Wasser zubereitet, anschließend in verdünnte, ausgekühlte Salzsäure (500 ml konz. chlorfreie HCl + ca. 400 ml H_2O) gegossen und auf 1000 ml aufgefüllt. In dieser Lösung besteht bei Zimmertemperatur keine Gefahr der Polymerisation der Zirkonium-Ionen. Wenn die Zirkonium-Lösung aus Zirkoniumnitrat zubereitet wird, ist es notwendig, die entsprechende Menge in Chlorid überzuführen, ohne daß sich nach dem Abdampfen der Stickoxyde infolge zu hoher Temperatur das in der Salzsäure unlösliche Zirkoniumoxyd bildet.

Die Zr-ECC-Lösung wurde durch Pipettieren der Zr-Lösung in einen Trichter mit kleiner Ausgangsöffnung, aus welcher sie langsam in dasselbe Volumen einer vollkommen gemischten ECC-Lösung zuläuft, hergestellt. Sie ist nach 24–30 St. gebrauchsfähig. Die Hydroxyd-Lösung wurde durch Auflösen von 19,0 g KOH in 50 ml Lösungsvolumen zubereitet.

RESULTATE

Allgemeine Ergebnisse

Die erhaltenen Absorptionsspektren von ECC und Zr-ECC bei ECC-Überschuß stimmen mit den Angaben der Literatur[2,3] überein. Die Absorptionskurve des Lackes ist jedoch in diesem Fall durch den Überschuß des freien Farbstoffes, welcher nach der Zersetzung von Zr-ECC durch die Fluoride noch wächst, verwischt. Aus der Figur 1, in welcher auch die Spektren des Lackes bei Zirkonium-Überschuß enthalten sind, ist ersichtlich, daß die Wellenlänge des Absorptions-Maximums von Zr-ECC bei 530 mμ und die des größten Unterschiedes in der Färbung des Farbstoffes und seines Lackes und des größten Entfärbungseffektes der Fluoride bei 540 mμ liegt. Thatcher[3] fand bei zwei verschiedenen ECC Präparaten bei 520 bzw. 540 mμ die größte Einwirkung der Fluoride.

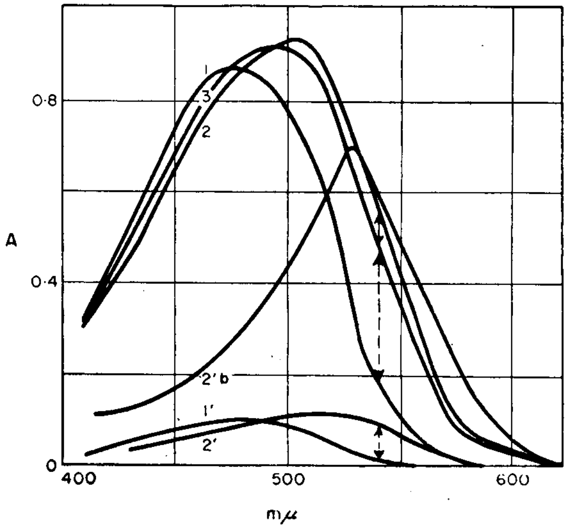

FIG. 1. Absorptionsspektrum von ECC und Zr-ECC in 0,2 n HCl

1. 90 μmol ECC,
2. 90 μmol ECC + 18 μmol Zr^{IV},
3. 90 μmol ECC + 18 μmol Zr^{IV} + 4,8 μmol F^-,

1'. 9 μmol ECC
2'. 9 μmol ECC + 18 μmol Zr^{IV},
2'b. 9 μmol ECC + 180 μmol Zr^{IV}.

Photometriert in Küvetten von 1 cm Meßlänge. Weitere Angaben sind aus der Arbeitsvorschrift ersichtlich.

In 0,1 n Salzsäure beträgt nach Megregian[2] das molare Verhältnis von Zr:ECC im Lack 1:3, bei höherer Azidität ist dieses Verhältnis wahrscheinlich infolge der Dissoziation des Lackes verwischt. In 0,2 n Salzsäure zersetzen 4,8 mμ F^-, wenn man nach dem Verlauf der Absorptionskurven urteilt, eine ungefähr 5,5 mμ gebundenem Zirkonium entsprechende Menge an Lack. Das Reaktionsverhältnis von F:Zr ist also unter diesen Bedingungen ungefähr 1:1. Diese Tatsache stimmt damit überein, daß das Ion ZrF^{3+} das stabilste System von Fluor und Zirkonium ist,[6] und erklärt die hohe Empfindlichkeit der Zr-ECC-Methode.

Die Neigung der Eichkurve ändert sich schon bei relativ kleinen Temperaturunterschieden der photometrierten Lösungen (siehe Figur 2) und beim Gebrauch verschiedener Zr-ECC-Lösungen, auch wenn sie auf dieselbe Weise aus demselben Präparat zubereitet wurden. Die Wahl des Bezugspunktes der Eichkurve und die Art der Bestimmung deren Verlaufes beeinflußt infolge der erwähnten Umstände markant die Reproduzierbarkeit der analytischen Resultate. Die meisten Autoren,[2,3,7,8] welche die vorliegende Methode verbesserten, bestimmten deshalb den Bezugspunkt und die Eichkurve anders.

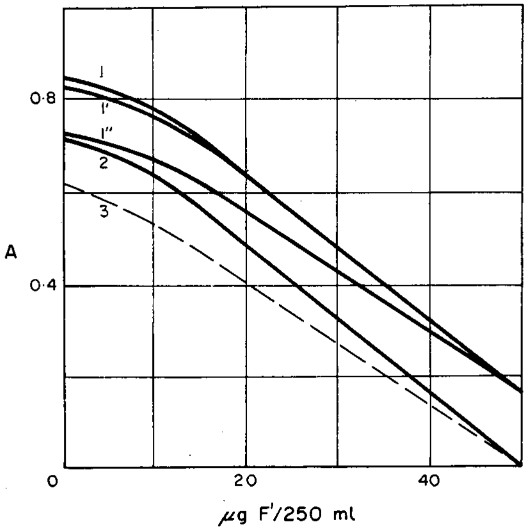

FIG. 2. Eichkurven von Fluor in 0,2 n Säure

1. HCl + $HClO_4$ (1,5 + 1),
2. HCl, gemessen gegen 50 µg F 250 ml in 0,2 n HCl,
3. HCl + 15 mg Triäthanolamin in 250 ml, photometriert gegen eine auf gleiche Weise zubereitete Lösung von 50 µg F, Messungen bei 21°,

1′, 1″, Messungen bei 24° und 31°. Sonstige Daten wie bei 1. Die weiteren Angaben sind aus der Arbeitsvorschrift ersichtlich.

Die Genauigkeit der Bestimmungen von Fluor in den Proben wird am wenigstens beeinflußt, wenn man eine Standardlösung von Fluor, deren Fluorgehalt einem passenden Punkt am Ende des linearen Verlaufes der Eichkurve entspricht, als Bezugslösung wählt, und wenn man die Resultate berücksichtigt, welche beim Studium des Störeffektes der Sulfate festgestellt wurden. Diesen Ansprüchen entspricht am besten eine Lösung mit 50 µg F/250 ml. Weiter ist es notwendig, bei jeder Serie von Bestimmungen die Neigung der Eichkurve mit einigen weiteren Standardlösungen nachzuprüfen und bei der Zugabe von Zr-ECC zur Analysenlösung gründlich zu mischen.

Die Extinktionswerte verschiedener Anteile einer 25 µg F/250 ml Standardlösung, welche in erwähnter Weise photometriert wurden, variierten meistens um ±0,010, d.h. um ±3%.

Genügend stabil wird die Farbintensität der Lösungen eine halbe Stunde nach der Vereinigung der Reaktanten.

Die Empfindlichkeit der Zr-ECC-Methode ist nach der unten angegebenen Arbeitsvorschrift annähernd 7 × größer als in der ursprünglichen Modifikation.[2] Bei Benutzung des Photometers Spekker wird sie um ungefähr $\frac{1}{3}$ vermindert.

Störeffekt der Sulfate, Bikarbonate und Kieselsäure

Aus Tabelle 1 ist ersichtlich, daß bei der Fällung der Sulfate aus neutralem Milieu Fluorverluste entstehen, welche mit wachsender Fluor-Konzentration steil und mit wachsendem Sulfatüberschuß mäßig ansteigen. Die Verluste lassen sich auch durch Fällen des Bariumsulfates aus 1 %igen Lösungen von Kaliumnitrat nicht vermindern, obwohl beide Ionen dieses Salzes vom Niederschlag leicht adsorbiert werden.[9] Man muß deshalb annehmen, daß die beobachteten Verluste hauptsächlich durch Mitfällung des wenig löslichen Bariumfluorides mit dem Bariumsulfat verursacht werden.

TABELLE 1.—DER EINFLUß DER F^-– UND SO_4^{2-}–KONZENTRATION AUF DIE FLUORVERLUSTE BEIM FÄLLEN DES BARIUMSULFATES AUS NEUTRALEM MILIEU

gegeben in 100 ml		%-Fehler der gefundenen Fluormenge	Gewichtsverhältnis SO_4^{2-}/F^-	%-Fehler · 10^{-3} SO_4^{2-}/F^-
F^-, *µg*	SO_4^{2-}, *mg*			
12	2	0	165	0
12	20	+ 8	1650	+5
20	2	−15	100	−150
20	40	−37	2000	−18
90	2	−11	22	−500
90	40	−50	450	−110

Die oben angedeutete Modifikation der Zr-ECC-Methode wurde so ausgearbeitet, daß man das Fluor mit vollkommen genügender Empfindlichkeit in Lösungen bestimmen kann, in welchen bei der Fällung von Bariumsulfat keine Fluorverluste entstehen.

Obwohl in neutralen Lösungen von Natriumfluorid und Natriumsulfat bis zur Konzentration von ungefähr 50 µg F/250 ml das Fluor-Ion mit dem Bariumsulfat nicht mitgefällt wird, traten in Lösungen, welche dieselbe Fluorkonzentration enthalten, Verluste ein, wenn in ihnen Bikarbonate neutralisiert wurden, wie sie der Zusammensetzung starker Bikarbonat-Mineralwässer entsprechen. Die Verluste kann man durch Fällen des Bariumsulfates aus sauerer Lösung vermeiden. Infolge des erhöhten Dampfdruckes von Fluorwasserstoff, in dessen Form das Fluor bei niedrigen Konzentrationen vorwiegend flüchtig ist,[10] und der höheren Löslichkeit des Bariumsulfates im saueren Milieu (z.B. werden in 0,02 n HCl 7 mg $BaSO_4$/l. gelöst[9]), ist es aber notwendig, die Azidität der Lösung, aus der Sulfat in der Nähe desSi edepunktes gefällt wird, möglichst niedrig zu erhalten.

Zu diesem Zweck war eine Lösung von ungefähr 0,02 n Salzsäure und 0,02 n Bariumchlorid am geeignetsten. Da aber kleine Sulfatmengen unter diesen Bedingungen so langsam gefällt werden, daß positive Fehler entstehen, ist es notwendig, den Sulfatgehalt vor der Fällung auf mindestens 20 mg in 200 ml zu erhöhen.

Bei der Neutralisation einer Lösung von 20 µg F und 350 mg Bikarbonaten in 250 ml mit Salzsäure, welche 200 mg Chloride enthielt, erhöhte sich der gefundene Fluorgehalt je nach der Qualität der Säure um 5–10 %. Diese Verschiebung des Resultates entsteht dadurch, daß die Chloride mit Zirkonium[6] oder sogar mit Zirkonyl (siehe Fig. 2) schwache Komplexe bilden, und daß in der verwendeten Salzsäure wechselnde Spuren von Flußsäure enthalten sind. Ersatz der Salzsäure durch Perchlorsäure, von der keine Komplexe mit Zirkonium bekannt sind, bewährte sich nicht, weil wahrscheinlich der Störeffekt des unvollständig gefällten Sulfates in Perchlorsäure durch das Fehlen der Konkurrenz der Chlorionen größer ist.

Für ausnahmsweise vorkommende Bikarbonatüberschüsse von 4 und mehr Größenordnungen ist es also notwendig, mit Hilfe von fluorfreien Bikarbonat-Präparaten Korrekturnomogramme zur Eliminierung des Einflusses der gebrauchten Salzsäure zu ermitteln. Ein einfacher Korrekturfaktor ist unbrauchbar, da der Einfluß der Chloride mit sinkendem Fluorgehalt anwächst.

Das direkte Ansäuern einer Lösung von 1 mg F^- und 50 mg SiO_3^{2-}/l. verursacht keine größeren Fehler (−5%) der Fluorbestimmung. Wenn aber in einer solchen Lösung nach dem Verdünnen Sulfat ausgefällt wird, können prinzipielle Fehler entstehen, welche mit Vergrößerung des Sulfatgehaltes anwachsen. Diese ziemlich variablen Fehler betrugen bei 2000-fachen Sulfatüberschuß gegenüber den Fluoriden bis zu −36%. Verursacht wurden sie wahrscheinlich durch Mitreißen des im sauren Milieu entstandenen Kieselsäure-Gels mit daran adsorbierten Fluoriden durch den Bariumsulfatniederschlag. Verhindern kann man sie dadurch, daß man die Lösungen, bevor sie angesäuert werden, verdünnt und einige Stunden erwärmt, wodurch das Fluosilikat wahrscheinlich zersetzt wird.

Störeffekte der Aluminium- und Eisen/III/-*Ionen und der Phosphate*

Die Beseitigung des Störeffektes von Aluminiumionen wurde durch Analysen von Lösungen verfolgt, in welchen das Aluminium mit Fluor wenigstens 3 Tage bei pH 3–5 reagieren konnte. In Lösungen vom pH 2, denen die Aluminium-Ionen erst knapp vor der Analyse oder sogar erst nach der Beimischung des ausgenützten Chelates[11] zugesetzt wurden, konnte man nämlich beobachten, daß der verursachte Störeffekt mit der Zeit wächst. Am besten gelang es, die Fluoaluminate auch bei genügend großem Aluminiumüberschuß nach Fällung der Sulfate bei einem pH-Wert von annähernd 13 zu zerlegen. Unter den Bedingungen der photometrischen Bestimmung (pH 1) kommt es dann nicht mehr zu ihrer Rekombination. Näheres ist aus der Arbeitsvorschrift ersichtlich.

Größere Mengen von Eisen(III)-Ionen, welche bei dem vorgeschlagenen Verfahren vor allem beim Alkalisieren aus den gegebenenfalls enthaltenen Eisen(II)-Bikarbonaten entstehen, bilden mit ECC ein ähnlich gefärbtes Chelat wie Zirkonium. Negative Fehler, welche auf diese Weise auch bei einem Nullgehalt an Fluor entstehen, kann man am besten verhindern, indem man die Abscheidung von Eisen(III)-Hydroxyd nach Entweichen des Kohlendioxydes abwartet. Das Fluorid wird von dem langsam entstehenden Niederschlag nach fremder[12] und eigener Erfahrung nicht adsorbiert.

Von den Reagenzien, welche zur Tarnung oder Reduktion der Eisen/III/-Ionen benutzt werden, hat sich Triäthanolamin am besten bewährt. Da es aber die Neigung der Eichkurve bzw. die Empfindlichkeit der Bestimmung von Fluor (siehe Fig. 2) infolge der Bildung schwacher Zirkoniumkomplexe verringert und noch weitere Komplikationen verursacht, ist es besser, das oben angegebene Verfahren zu gebrauchen.

Die in Wässern meistens in kleineren Mengen als die Fluoride enthaltenen Phosphate stören die Fluorbestimmung weniger bei niedriger Temperatur und in saurer

Lösung,[3] vor allem von Salzsäure. Der Störeffekt der Phosphate wird deshalb durch Kühlen und Ansäuern der Lösung vor Zugabe des Zr-ECC vermindert. Aber auch nach dem Ansäuern ist es notwendig, die sauere Zr-ECC-Lösung gleich zuzugeben, damit die in der vorgeschlagenen Modifikation höchstmögliche Konzentration an Wasserstoff-Ionen in der Lösung bald erzielt wird. Bei diesem Verfahren besteht auch nicht die Gefahr der Rekombination der Fluoaluminate.

TABELLE 2. EINFLUß EINER REIHE VON KOMPONENTEN AUF DIE BESTIMMUNG DES FLUOR-GESAMTGEHALTES

gegeben 1 mg F/l. und mg/l. von				gefunden mg F/l.
4000 SO_4^{2-},	3500 HCO_3,	2500 K^+,	1300 Na^+	1,05
4000 SO_4^{2-},	1000 Ca^{2+}, 1200 Cl^-,	200 K^+,	1300 Na^+	1,04
4000 SO_4^{2-},	100 SiO_3^{2-}			0,95
1000 SO_4^{2-},	4 Al^{3+}			1,03
40 Fe^{2+},	1500 HCO_3^-		sat. CO_2	0,96
	analysiert 1 Woche nach der Zubereitung			
1,3 PO_4^{3-}		1,05	2 $B_4O_7^{2-}$	1,02
2,6 PO_4^{3-}		1,14	50 NO_3^-	1,04
5,2 PO_4^{3-}		1,60	8 Al^{3+}	0,96
2 AsO_4^{3-}		1,02	2 Mn^{2+}	1,02
10 AsO_4^{3-}		1,22	2,Be^{2+}	1,00

Die Bestimmungen wurden auf der Grundlage der im Text folgenden Arbeitsvorschrift nach Ansäuern ungefähr 18° warmer alkalischer Lösungen durchgeführt.

ARBEITSVORSCHRIFT

Nach dem Absetzen des Eisenhydroxydes pipettiert man aus den klaren Anteilen der hoch mineralisierten Wässer ein entsprechendes Volumen (z.B. aus einer Lösung von ca. 1 mg F/l. 25 ml). Dieses verdünnt man auf 200 ml und erwärmt es 3 h bei 40° bzw. läßt es nach Erwärmen über Nacht stehen. Der Sulfatgehalt der Probe wird mit einer Natriumsulfatlösung auf mindestens 20 mg in 200 ml eingestellt. Nach Aufkochen wird die Lösung mit 0,5 n Salzsäure neutralisiert und mit 3,0 ml überschüssiger Säure versetzt. Sulfat wird unter ständigem Rühren mit 25 ml einer 2%-igen saueren (5 ml konz. HCl/1) Bariumchloridlösung gefällt, die Lösungen zum Sieden gebracht, ungefähr 8 h auf 60° erwärmt und nach Auskühlen in einem 250 ml Meßkolben zur Marke aufgefüllt und gemischt.

24–48 h nach der Fällung werden 20 ml der klaren Lösung in ein 50 ml Becherglas pipettiert, mit 0,25 ml Kaliumhydroxyd-Lösung versetzt (mit Hilfe einer 1 ml Bürette) und 1 h auf 40° erwärmt. Anschließend werden bei elektromagnetischer Mischung schnell 0,25 ml konz. Salzsäure und 1,5 ml Zr-ECC-Lösung zugegeben. Hierbei muß—vor allem bei erhöhter Phosphat-Konzentration—stark gekühlt werden.

Nach 45–75 min wird die Lösung in Küvetten von 4 cm Meßlänge gefüllt und bei 540 mμ gegenüber einer gleich verarbeiteten Eichlösung von 50 μg F/250 ml photometriert. Die Resultate wertet man mit Hilfe einer Eichkurve aus, deren Verlauf man während jeder Bestimmungsserie mittels vier weiterer Eichlösungen nachprüft.

Während 8 Arbeitsstunden, welche meistens über 3 Tage verteilt sind, kann man ungefähr 15 Bestimmungen durchführen. Das vorgeschlagene Verfahren ist deshalb bei einer größeren Anzahl von Bestimmungen zeitsparender als die Bestimmung von Fluor mit ECC in stark mineralisierten Wässern nach vorangehender Abtrennung.[2]

Bei ungefähr 200 analysierten Proben von stark mineralisierten Wässern (Rückstand 5 bis 20 g/l.) schwankten die Resultate relativ um ± 5 bis 10%, was bei einem Gehalt von 2 mg F/l. etwa ± 1 bis $2 . 10^{-3}\%$ F im Rückstand entspricht, was vollkommen hinreichend ist.

Im Vergleich mit einer großen Reihe von Methoden, von welchen nur die vor kurzem veröffentlichte Anwendung von Lanthan-Chloranilat[13] angeführt sei (bei der Sulfate, Chloride und Nitrate bis zum sechsmaligen Überschuß nicht stören und alle Kationen mit Ausnahme von Amonium-Ionen stören) ist das vorgeschlagene Verfahren also wesentlich besser. Auch im Bezug zu den älteren Modifikation- der Zr-Eriochromcyanin-Methode, die schon in der ursprünglichen Form von Megregian[2] die oft als Standardmethode[14,15] gebrauchte Bestimmung mittels Zr-Alisarin übertraf und ebenfalls von dem erwähnten Autor gründlich untersucht wurde,[16] ist das vorgeschlagene Verfahren vorteilhafter, da es eine einfachere und schnellere Bestimmung von Fluor (ohne Destillation) in relativ kompliziertem Material ermöglicht. Die erwähnten Vorteile, zu welchen auch die hohe Bestimmungsempfindlichkeit zählt, sind jedoch immer noch nicht so groß, daß ein weiteres intensives Ausfinden noch schnellerer Bestimmungsweisen für dieses physiologisch sehr aktive und ind der Erdrinde verhältnißmäsig reichlich enthaltene Element nutzlos werden dürfte.

Die vorliegende Studie weist wahrscheinlich auch auf die Grenzmöglichkeiten der analytischen Nützung von "klassischen" Farbstoffen (d.h. von Farbstoffen, welche keine sehr feste Chelate bilden) bei der Lösung des verfolgten Problems hin. Auf Grund der Erkenntnis dieser Möglichkeiten sowie der Eigenschaften einzelner störender Komponenten, die in dieser Arbeit während ihrer nacheinander folgenden Beseitigung ersichtlich wurden, wird in der Zukunft eine größere Aufmerksamkeit denjenigen Farbstoffen gewidmet, die sehr stabile Chelate bilden. Man kann nämlich erwarten,[17] daß sie eine noch einfachere Bestimmung von Fluor als das vorgeschlagene Verfahren ermöglichen. Nach einer erfolgreichen Lösung der angedeuteten Bestimmungsweise,[17] bei welcher manche Erfahrungen aus der vorliegenden Arbeit völlig ausgenützt werden (z.B. die Art der Feststellung der Eichkurve), wird das vorgeschlagene Verfahren als Kontrollmethode dienen. Bei den Analysen der glücklicherweise nur sehr selten vorkommenden Wässern mit ungewöhnlich hohem Sulfat-Gehalt (z.B. das Zaječice-Bitterwasser, Böhmen, enthält 23,8 g SO_4^{2-}/kg) wird es dann auch weiterhin notwendig sein, zur Fällung der Sulfate diejenigen Kenntnisse anzuwenden, die zum Kernpunkt der vorliegenden Arbeit wurden.

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Summary—A highly sensitive spectrophotometric and photometric method for the determination of fluoride is described, based on the decolorisation of the zirconium-Eriochromcyanine lake in 0·2*N* hydrochloric acid. Interference from large amounts of sulphate is prevented by precipitating sulphate from slightly acidic solution. In these conditions no co-precipitation of fluoride occurs even in solution high in bicarbonate and silicic acid. Fluoaluminate is decomposed by alkali. The formation of an interfering iron^{III} dye complex is prevented by allowing the precipitation of ferric hydroxide after carbon dioxide is expelled.

Résumé—Les auteurs décrivent une méthode spectrophotométrique et photométrique très sensible pour le dosage du fluorure; cette méthode est basée sur la décoloration de la laque zirconium-ériochromecyanine dans l'acide chlorhydrique 0,2 N. L'interférence de grandes quantités de sulfate est

empêchée en précipitant le sulfate en solution faiblement acide. Dans ces conditions, le fluorure ne précipite pas, même en solution concentrée en bicarbonate et acide silicique. Le fluoaluminate est décomposé par les alcalis. La formation d'un complex coloré gênant du fer (III) est empêchée en réalisant la précipitation de l'hydroxyde ferrique après avoir chassé l'anhydride carbonique.

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THE DETERMINATION OF TRACES OF RUTHENIUM IN SAMPLES OF PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A neutron-activation method has been developed for determining small amounts of ruthenium impurity in samples of platinum. The Harwell nuclear reactor BEPO has been used as the source of neutrons. The procedure depends on the chemical separation of radioactive ruthenium, with added ruthenium carrier, from irradiated samples and standards. Results are quoted for the ruthenium contents of a number of samples of platinum.

THE work described in this paper forms part of a research programme on the development of new methods for the analysis of trace impurities in precious metals.[1–5] Relatively little has been reported previously on the determination of ruthenium by neutron-activation analysis. Leddicotte *et al.*[6] of the Oak Ridge National Laboratory, U.S.A., have indicated that radioactivation has been applied to the determination of small amounts of ruthenium in lithium iodide and report concentrations of 1–3 ppm. Miller,[7] working at the same establishment, has written a report on neutron-activation analysis applied to elements of Periodic Group VIII; his dissertation provides some general information on the determination of ruthenium.

With a thermal neutron flux of 10^{12} neutrons/cm^2/sec, as is available in the Harwell Pile BEPO, it has been estimated[8] that *ca.* 10^{-9} g of ruthenium may be determined under ideal conditions. This is below the limits of sensitivity of most other analytical methods for determining the element.[9,10]

Neutron-activation of ruthenium

Naturally occurring ruthenium consists of seven isotopes: ^{96}Ru (5·57%), ^{98}Ru (1·91%), ^{99}Ru (12·7%), ^{100}Ru (12·7%), ^{101}Ru (17·0%), ^{102}Ru (31·5%) and ^{104}Ru (18·5%). Some of these isotopes give rise to radionuclides when subjected to irradiation with thermal neutrons. The production and decay of the radionuclides is represented by the following sequences:

$$^{96}\text{Ru}(n,\gamma)^{97}\text{Ru} \xrightarrow[t_{1/2} = 2\cdot88 \text{ day}]{\text{EC}} {}^{97m}\text{Tc} \xrightarrow[t_{1/2} = 91 \text{ day}]{\text{IT}} {}^{97}\text{Tc} \xrightarrow[t_{1/2} = 2\cdot6 \times 10^{6} \text{ yr}]{\text{EC}} {}^{97}\text{Mo}$$

$$^{102}\text{Ru}(n,\gamma)^{103}\text{Ru} \xrightarrow[t_{1/2} = 39\cdot8 \text{ day}]{\beta^-} {}^{103m}\text{Rh} \xrightarrow[t_{1/2} = 57 \text{ min}]{\text{IT}} {}^{103}\text{Rh}$$

$$^{104}\text{Ru}(n,\gamma)\,^{105}\text{Ru} \xrightarrow[t_{1/2} = 4\cdot5 \text{ hr}]{\beta^-} {}^{105m}\text{Rh} \xrightarrow[t_{1/2} = 45 \text{ sec}]{\text{IT}} {}^{105}\text{Rh} \xrightarrow[t_{1/2} = 36\cdot5 \text{ hr}]{\beta^-} {}^{105}\text{Pd}$$

Relevant thermal neutron-activation cross-sections, σ (barn), are:[11]

$$^{96}\text{Ru} \qquad \sigma = 0{\cdot}21$$

$$^{102}\text{Ru} \qquad \sigma = 1{\cdot}44$$

$$^{104}\text{Ru} \qquad \sigma = 0{\cdot}7.$$

Information on the decay of the radionuclides, including references to the original literature, is given by Strominger, Hollander and Seaborg.[12]

The absorption cross-section of platinum for thermal neutrons is high (8·8 barn) compared with that for ruthenium, (2·56 barn). To avoid shelf-shielding differences between samples and standards in the present work, standards were, therefore, prepared by the addition of small known quantities of ruthenium to analytical samples.

EXPERIMENTAL

Irradiation

Specimens of platinum sponge for analysis had been broken down to a powder and 0·1-g samples were accurately weighed and sealed in silica irradiation tubes of 4-mm internal diameter. Standards were prepared by the addition of weighed portions (*ca.* 0·05 g) of a standard solution of ruthenium (10 mg of ruthenium per litre of $3M$ hydrochloric acid) to 0·1 g samples of platinum in silica irradiation tubes. The liquid was allowed to soak into the metal powder, then was carefully evaporated to dryness, after which the tubes were sealed.

Samples, together with standards containing added ruthenium, were packed in silica wool in standard aluminium screw-top cans and were sent to the Atomic Energy Research Establishment, Harwell, for neutron activation. Irradiations were for a period of 1 week in the nuclear reactor BEPO with a thermal neutron flux of $1{\cdot}2 \times 10^{12}$ neutrons/cm²/sec.

Radiochemical procedure

In the radiochemical procedure for the separation of ruthenium from samples and standards following neutron irradiation, inactive ruthenium was employed as a carrier. The material used for the carrier was checked for freedom from radioactive contamination, because ruthenium produced in recent years has been shown to contain ^{106}Ru from "fall-out" from nuclear explosions.[13]

Many radiochemical procedures for ruthenium are available and a number of them are appended in a recent monograph on the radiochemistry of the element.[14] However, a new procedure utilising solvent extraction and based in part on the work of Surasiti[15,16] was developed for the present study.

Special reagents

Ruthenium carrier:[17] Dissolve 0·75 g of ruthenium chloride* in 50 ml of water, then add 5 g of sodium hydroxide and 2 g of potassium persulphate. Heat to boiling. When the precipitate has dissolved, add 0·5 ml of methyl alcohol and stir thoroughly. Digest the mixture near the boiling point until the precipitate coagulates, then centrifuge the solution and discard the supernate. Wash the precipitate once with boiling water and dissolve it in 50 ml of hot $2{\cdot}5M$ sodium hydroxide solution containing 2 g of potassium persulphate. Cool and dilute to *ca.* 100 ml. Add 2 ml of the prepared carrier solution to 5 ml of potassium periodate-potassium hydroxide reagent (see below) in a 50 ml calibrated flask and dilute to volume. Measure the optical absorbancy of this solution in a 1-cm cell at 4700 Å. Dilute the ruthenium carrier solution by proportion so that the absorbancy of a 2-ml aliquot in the alkaline periodate reagent lies between 0·6 and 0·8. Prepare a calibration chart using 0·5, 1·0, 1·5, and 2 ml of the final ruthenium carrier solution to determine the optical absorbancy.

Potassium periodate-potassium hydroxide reagent: Dissolve 20 g of potassium hydroxide and 10 g of potassium periodate in 200 ml of water.

Osmium carrier: Dissolve a weighed quantity of pure recrystallised ammonium hexachloro-osmate in dilute hydrochloric acid to give a solution containing 1 mg of osmium/ml.

Gold carrier: Prepare a solution containing 1 mg of gold/ml in dilute hydrochloric acid.

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* Beta-count this material for a considerable period to ensure its freedom from ^{106}Ru — ^{106}Rh.

Carbon tetrachloride: Shake analytical reagent material with 0·1N potassium permanganate in 2M sulphuric acid for several hr. Separate the phases and shake the carbon tetrachloride with several portions of concentrated sulphuric acid and once with water. Saturate the carbon tetrachloride with chlorine and reflux for a few hr. Remove chlorine by shaking with several portions of 2M potassium hydroxide. Wash the carbon tetrachloride with water until neutral to litmus paper, dry with Anhydrone, and distil. Store in the dark.

Silver$^{\text{II}}$ oxide: Prepare this by boiling a solution of silver nitrate with a strong potassium hydroxide solution of potassium persulphate until evolution of oxygen ceases, wash with hot water, and dry over a desiccant.

Separation procedure

Dissolution of the irradiated platinum. Remove the irradiation tubes from the can, open them, and transfer the samples and standards quantitatively to 150-ml beakers each containing 2 ml of standard ruthenium carrier and 3 ml of 12M hydrochloric acid. In every case wash out the tube thoroughly with hot 6M hydrochloric acid and add the washings to the respective beaker. Add 1 ml of 16M nitric acid to the contents of each beaker and slowly dissolve the platinum by warming on a hot-plate. When the platinum has dissolved, add two successive 1-ml portions of 12M hydrochloric acid and heat to remove nitric acid.

Removal of osmium. Add 1 ml of osmium carrier and 15 ml of 6M sulphuric acid and evaporate to fumes. Continue fuming moderately for *ca.* 1 hr. Cool and transfer the solution to a 50-ml centrifuge tube containing 15 ml of water. Cool and add 0·1N potassium permanganate solution until a pink colour remains. Destroy excess permanganate by adding 50 mg of iron$^{\text{II}}$ ammonium sulphate hexahydrate dissolved in a little water. Without delay add 15 ml of 16M nitric acid and extract osmium tetroxide into three successive 10-ml portions of carbon tetrachloride. Separate and discard the organic layers, retaining the aqueous phase.

Oxidation and extraction of ruthenium. Add, with stirring, sufficient silver$^{\text{II}}$ oxide to the aqueous solution to give a brown colour. Allow to stand for 10 min to ensure complete oxidation of ruthenium to the tetroxide. Extract with three 10-ml portions of carbon tetrachloride. Combine and retain the organic layers in a clean 50-ml centrifuge tube. Wash the combined extract twice with 10-ml portions of 2M sulphuric acid containing a little silver$^{\text{II}}$ oxide. Separate the organic phase and discard the wash solutions. Return ruthenium from the organic phase to aqueous solution by agitating the carbon tetrachloride extract with 10 ml of 3M sodium hydroxide solution to which has been added 2 drops of 5% sodium dithionite solution. Separate the aqueous layer into a clean 50-ml centrifuge tube.

Removal of gold. Acidify the solution with hydrochloric acid, add 1 ml of gold carrier, and extract the gold with three 10-ml portions of ether. Retain the aqueous phase and make it alkaline with 6M sodium hydroxide solution.

Precipitation of the ruthenium for counting. Add 2 ml of industrial methylated spirit and mix thoroughly, Digest on a stream bath until the precipitate of ruthenium dioxide has coagulated. Centrifuge and discard the supernate. Wash the precipitate with portions of water and alcohol. Slurry it with a little alcohol on to an aluminium counting tray using a dropping pipette fitted with a rubber bulb. Evaporate off the alcohol under a radiant-heater lamp. The precipitate is then ready for counting.

Determination of the chemical yield. After counting measurements on the final precipitates have been performed, determine the chemical yield for each sample and standard as follows. (This part of the procedure must be carried out strictly quantitatively and without loss). Remove the bulk of the ruthenium dioxide from a counting tray by tapping the solid into a 50-ml beaker. Dissolve the remainder using 5 ml of potassium hydroxide-potassium periodate reagent, allowing the reagent to flow slowly from a dropping pipette across the tray and into the beaker. Rinse the tray with a few drops of distilled water, and collect the washings in the beaker. Warm to complete solution if necessary and transfer quantitatively to a 50-ml calibrated flask and make to the mark with water. Measure the optical absorbancy at 4700 Å in a 1-cm cell. Obtain the chemical yield by reference to the absorbancies determined for known aliquots of the ruthenium carrier solution.

Measurement of radioactivity of the final precipitates

The final precipitates of ruthenium dioxide from the irradiated samples of platinum and from the standards were counted under similar conditions with a Geiger-Müller counter of the EHM 2/S type. All measured counting rates were corrected for paralysis, background, and chemical yield and for any decay of significance between counting samples and standards.

The radiochemical purity of the sources was checked by decay and gamma-spectrometric measurements. The measured γ-ray energies and half-lives corresponded with those obtained from a sample of neutron-irradiated pure ruthenium.

RESULTS

In Table I are shown results of analyses of samples of platinum. No ruthenium could be detected in these specimens by emission spectrographic analysis.

TABLE I.—RUTHENIUM CONTENTS OF SAMPLES OF PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample	Ruthenium content, *ppm*
Pt 1	1·03, 1·07
Pt 2	1·96, 1·92
Pt 3	0·83, 0·86
Pt 4	0·97, 0·93
Pt 5	1·61, 1·50, 1·70, 1·51
Pt 6	1·09, 1·12
Pt 7	1·75, 1·78

DISCUSSION

In the neutron-activation analysis of ruthenium in samples of platinum consideration must be given to the possibility of formation of radionuclides used in the analysis from activation of elements other than ruthenium in the samples.

Thus possible interference might arise from the following nuclear reactions of rhodium and palladium:

$$^{103}\text{Rh}(\text{n, p})^{130}\text{Ru}$$

$$^{106}\text{Pd}(\text{n}, \alpha)^{103}\text{Ru}$$

$$^{108}\text{Pd}(\text{n}, \alpha)^{105}\text{Ru}.$$

These reactions could occur with the fast flux of neutrons associated with the thermal neutron flux within the reactor BEPO. Under the irradiation conditions employed in the present work this fast neutron flux was 2×10^{11} neutrons/cm^2/sec. Interference from the nuclear reactions was shown to be unimportant, however, by analysing by activation samples of platinum Pt 6 to which had been added 0·3 μg of rhodium and 0·3 μg of palladium. The results obtained were 1·02, 1·05, 0·99 and 1·09 ppm of ruthenium which agree well with the analyses of platinum Pt 6 listed in Table I.

Possible interference from the nuclear reactions:

$$\text{U}(\text{n, f})^{103}\text{Ru}$$

$$\text{U}(\text{n, f})^{105}\text{Ru}$$

$$\text{U}(\text{n, f})^{106}\text{Ru}$$

has been discounted because the samples of platinum analysed are unlikely to contain more than negligible amounts of uranium.

Acknowledgement—We are grateful to The International Nickel Company (Mond) Ltd., for the supply of precious metals, for financial support, and for a Research Fellowship to one of us (R. A. K.).

Zusammenfassung—Eine auf Neutronenaktivierung beruhende Methode zur Bestimmung von Rutherniumspuren in Platin wurde entwickelt. Der Harwell-Reaktor BEPO diente als Neutronenquelle. Radiochemische Trennungen nach Zugabe von Ruthenium als Träger, wurden auf Probe und Standard angewandt. Resultate für einige Proben werden mitgeteilt.

Résumé—Les auteurs ont mis au point une méthode de dosage, par activation neutronique, de faibles quantités d'impureté de ruthénium dans des échantillons de platine. Le réacteur nucléaire BEPO de Harwell a été utilisé comme source de neutrons. La méthode dépend de la séparation chimique du ruthénium radioactif, à l'aide d'un entraîneur, des échantillons irradiés et des étalons. Les résultats cités donnent les teneurs en ruthénium d'un certain nombre d'échantillons de platine.

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AN INVESTIGATION OF SODIUM 5-(3-NITROPHENYLAZO)SALICYLATE AS A SPECTROPHOTOMETRIC REAGENT FOR MAGNESIUM

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Summary—Sodium 5-(3-nitrophenylazo)salicylate reacts almost specifically with magnesium ions (at pH 10·5) to give a yellow coloured chelate. The solution has an absorbance maximum at 450 mμ. The sensitivity of the reaction is 0·01 μg of magnesium per cm^2 for log $I_0/I = 0{\cdot}001$. Optimum conditions for the reaction have been established. Development of the spectrophotometric method for the determination of magnesium included a study of the effect of pH, the ratio of reagent to magnesium, photometric stability of the complex, its conformity to Beer's law, and the rate of colour formation. The method has been applied successfully to the determination of magnesium in silica brick and silicon-aluminium alloy.

A RECENT critical review[1] of the analytical chemistry of magnesium cites only three chelating agents suitable for its spectrophotometric determination. These are Eriochrome Black T,[2–5] 2-[2-hydroxy-3-(2,4-xylylcarbamoyl)]-1-naphthalazophenol[6] and its sulphate,[7] and 8-quininol.[8] Consequently, when the spot test procedure of Yoe[9] showed that sodium 5-(3-nitrophenylazo)salicylate reacted almost specifically with ammoniacal magnesium to give a yellow colour, it was decided to examine the nature of the complex and to assess its worth as a reagent for the spectrophotometric determination of magnesium.

EXPERIMENTAL

Apparatus

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

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

Reagents

Sodium 5-(3-*Nitrophenylazo*)*salicylate* (*NPAS*): Obtained from Eastman Kodak; the solid is brick red. In solution it acts as a pH indicator, being yellow below pH 10 and wine red above pH 12. (The colour change is not sufficiently sharp to make it a useful indicator). Below pH 9 its solubility is about 0·02 g/l., and at pH 10·5 it is about 0·065 g/l. Solutions continuously exposed to light are slightly unstable but those kept in polyethylene bottles in a cupboard are stable for at least 3 weeks. The solution used for routine determinations was about saturated and was prepared by weighing out 0·065 g of NPAS, adding 500 ml of pH 10·5 buffer (see below), making up to 1 litre and filtering into a polyethylene bottle. More dilute standard solutions were prepared for mole ratio determinations.

Standard Magnesium Solution: Magnesium oxide ("Baker analysed" A.C.S.) was ignited and cooled in a desiccator. 1·6582 g was dissolved in the smallest possible amount of hydrochloric acid and made up to 1 litre with triply-distilled water. This solution contained 1 g of magnesium as was confirmed by titrating with EDTA.

Buffer Solutions: (1) pH 10: Fisher standard buffer was used to set the pH meter for readings in the pH 10 region. (2) pH 10·5: The sodium borate-carbonate mixture of Kolthoff and Vleeschhouwer[10] was used. A mixture of 89 ml of carbonate solution (5·3 g of anhydrous sodium carbonate/l.; 0·05*M*) and 11 ml of borax solution (19·1 g of borax/l.; 0·05*M*) has a pH of 10·5.

Solutions of Diverse Ions: Reagent grade salts were used to prepare solutions of various ions. The stock solutions generally contained 1 g of the ion per litre of solution.

Acetylacetone: Reagent grade acetylacetone was used as a 25% v/v solution in AnalaR carbon tetrachloride.

Water: Triply-distilled.

Nitric Acid: C.P., doubly distilled.

Hydrochloric Acid: AnalaR, distilled four times.

Ammonia: C.P. Other reagents were made up from the best quality material available and used without further purification.

DETERMINATION OF OPTIMUM CONDITIONS

Preliminary tests showed that at about pH 10·5 when the reagent solution is an orange-red colour, the magnesium complex is yellow. The absorption curves (Fig. 1) indicated that it should be possible to determine magnesium despite the high reagent absorption. Since the colour of the reagent is markedly pH dependent in the region of 10 to 12, changing its absorption peak from 372 mμ to 479 mμ (Fig. 2), it was expected that its magnesium complex would also be pH dependent.

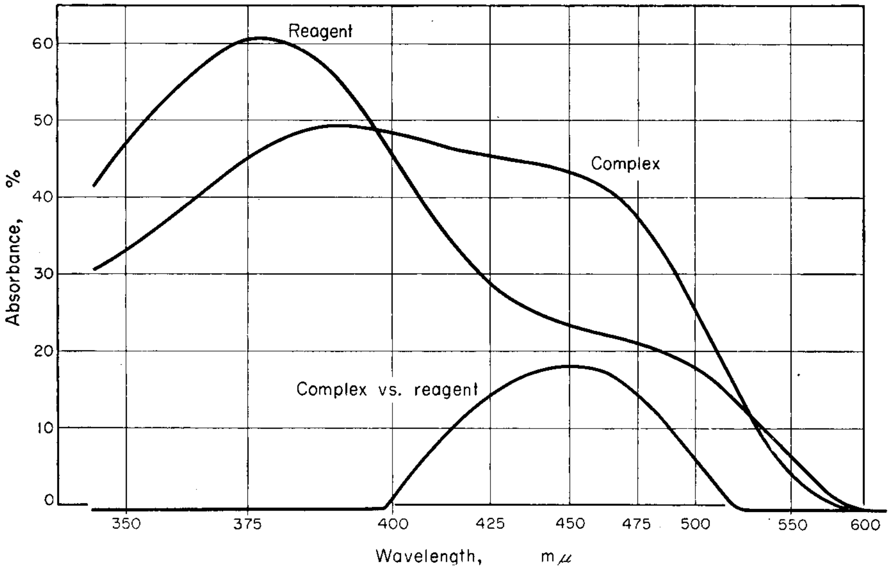

FIG. 1.—Absorption curves at pH 10·5 for reagent against water, complex against water, and complex against reagent.

Effect of pH

Fig. 2 shows the dependence of the complex on pH ("apparent" pH) in a buffered solution. In an unbuffered solution a curve of similar shape was obtained with the peak at pH 10·2. This might be because an increase in ionic strength hinders the formation of the magnesium complex as it does the precipitation of magnesium hydroxide. The sharp fall off in absorption is almost certainly caused by hydroxide precipitation. However, other conditions affect the choice of optimum pH. It is preferable that the reagent absorption at 450 mμ be constant for small changes in pH. This condition is best realised at pH 10·5. The buffer system employed required that the pH be adjusted by hydroxide addition to a value close to that of the final pH. The possibility of hydroxide precipitation before complex formation increases, therefore, with a higher final pH value. Furthermore, since a carbonate-borate buffer is preferred, a higher pH means a higher carbonate concentration, with greater chance of calcium interference. Hence pH 10·5 was adopted as a working pH, with some loss in sensitivity and flexibility. All pH values are uncorrected for ionic concentration.

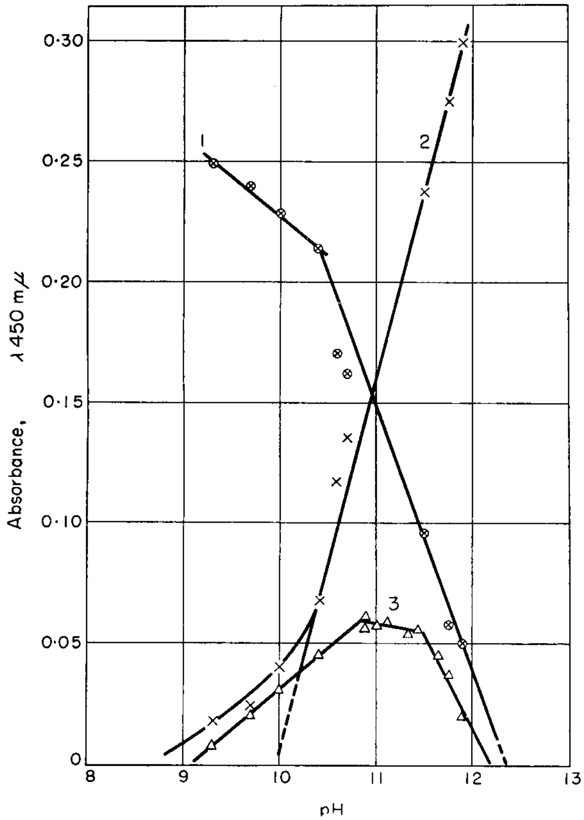

FIG. 2.—(1) Absorption of reagent at 372 mμ against pH,
(2) absorption of reagent at 479 mμ against pH,
(3) complex absorption at 450 mμ against pH.

Choice of buffer

Following the preceding argument, one might ask why either a Sörensen glycine–sodium chloride–sodium hydroxide buffer or an ammonia–ammonium chloride buffer was not employed. In the presence of a Sörensen buffer, calcium interferes by forming a coloured complex. The use of the ammonia buffer enhanced phosphate interference and slightly lowered the sensitivity of the method. As will be discussed later, the carbonate buffer is tolerant towards these interferences. If the sample is calcium-free, the Sörensen buffer would be suitable.

Order of addition of reactants

In the absence of alkaline earth ions the order of addition of the three reactants, magnesium, NPAS and buffer, does not matter. If the alkaline earths are present, the NPAS and buffer must be mixed before being added to the sample solution. This is necessary because the addition of carbonate buffer to the solution of the magnesium and alkaline earths, either before or after the addition of NPAS, results in turbidity or precipitation.

Stability of colour

The colour is formed rapidly and is fairly stable. The absorption falls off by about 1% after 1 hr and 13% after 4 days.

Beer's law and sensitivity

The range over which Beer's law is obeyed varies with the conditions and the amount of reagent used. With the recommended amount the range is from 0·05 to 2·5 ppm of magnesium in pure solutions. If the solution is treated extensively beforehand, *e.g.*, by repeated precipitations or extractions, the range may fall to 0·05–1·0 ppm; but the sensitivity remains the same and is 0·01 μg of magnesium per cm² for $\log I_0/I = 0{\cdot}001$. As can be seen from the mole ratio curve, (Fig. 3), the absorbance continues to increase with further addition of magnesium. The curve is linear up to 8 ppm and the sensitivity in this range is 0·38 μg of magnesium/cm². If two thirds of the reagent concentration is used, the sensitivity is approximately halved whilst the range is nearly doubled. The extent to which the sensitivity may be increased by increasing the reagent concentration is limited by its solubility and absorption at 450 mμ.

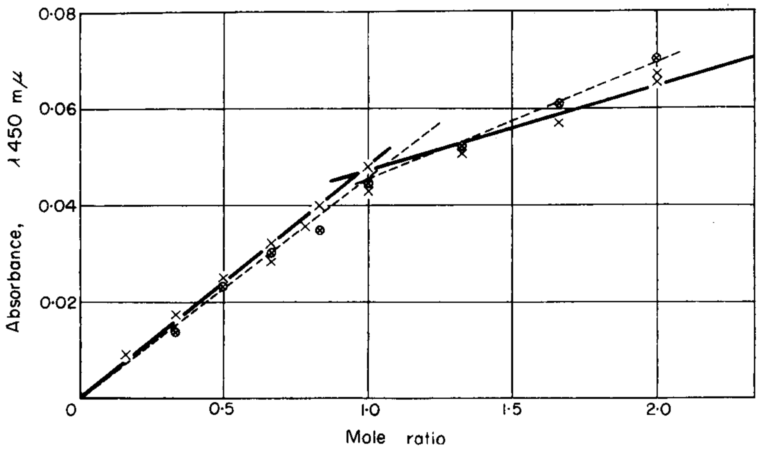

FIG. 3.—Mole ratio and "reverse" mole ratio:
⊗ = 3 × 10⁻⁷ moles of magnesium with varying amounts of NPAS.
× = 3 × 10⁻⁷ moles of NPAS with varying amounts of magnesium.

Structure of the magnesium complex

The mole ratio method of Yoe and Jones[11] (Fig. 3) and Job's[12] method of continuous variations as modified by Vosburgh and Cooper[13] (Fig. 4) indicates a 1:1 complex. The reagent is too insoluble and too intensely coloured to permit the use of the Harvey and Manning[14] slope-ratio method, which requires a large constant excess. But the "reverse" mole ratio method adopted (Fig. 3) indicates (by the absence of breaks) no higher complexes. Mole ratio studies also indicate that the complex is weak. EDTA readily destroys the complex but the colour change involved is not sufficiently sharp to warrant using NPAS as an indicator in the EDTA titration of magnesium. The second pK value[15] for salicylic acid is about 13. Hence

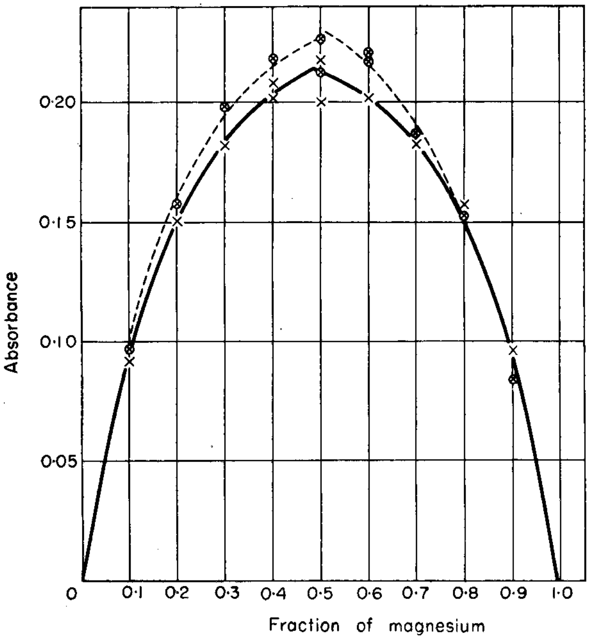

FIG. 4.—Continuous variations (15 × 10^{-5} M; pH 10·4): × = 440 mμ: ⊗ = 475 mμ.

it seems reasonable to postulate the structure of the chelate as shown in Fig. 5. Waters of co-ordination almost certainly take up the remaining co-ordination positions.

Effect of diverse ions

The reagent was tested on the spot plate with seventy-eight different ions, buffered at pH 10·5. Only calcium formed a colour with the reagent. Quantitative estimates of interferences were made by adding the interfering ion to a magnesium solution, which was then analysed by the proposed procedure. This showed that although only calcium gives a colour, every ion which was present in sufficient concentration to precipitate at pH 10·5 caused an error, either by coprecipitation or by turbidity. Hence most cations must be removed from solution before determining the magnesium.

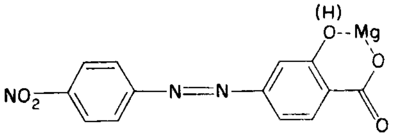

FIG. 5.—Proposed structure of the magnesium complex of 5-(3-nitrophenylazo)salicylic acid (waters of co-ordination omitted).

When magnesium is present at a concentration of 1 ppm, phosphate up to 100 ppm does not cause more than 10% interference. If present at a concentration of 0·5 ppm, less than 10% interference is caused by 0·1M chloride, 0·01M sulphate, 0·01M acetate, 0·01M nitrite and 0·001M nitrate, respectively. The molarities refer to the final solution.

Interference of alkaline earths

The effects of the alkaline earths upon the reaction were so unusual that they were investigated more fully. In the presence of an ammonia or Sörensen buffer (*vide ultra*) the calcium complex absorbs at the same wavelength at which the magnesium complex absorbs but the sensitivity is only a tenth of that for magnesium. The effect of calcium on the absorption of the magnesium complex in the presence of a carbonate buffer is shown in Fig. 6. Barium and strontium behave similarly. The slight initial increase in absorption may be caused by either complex formation or turbidity from a suspension of finely divided calcium carbonate; the absorption lowering may be ascribed to the precipitation of the carbonate with coprecipitation of the magnesium. Because the system is not completely reproducible, the minimum amount of calcium needed to cause this type of interference could not be established precisely. Sometimes 20 ppm could be tolerated and other times it could not, but 40 ppm in every case caused a lowering of the absorption. It was found, however, that if calcium, strontium and barium are added at a level of 40 ppm each, the absorption remained constant and correct (Fig. 7). Further experiments showed that:

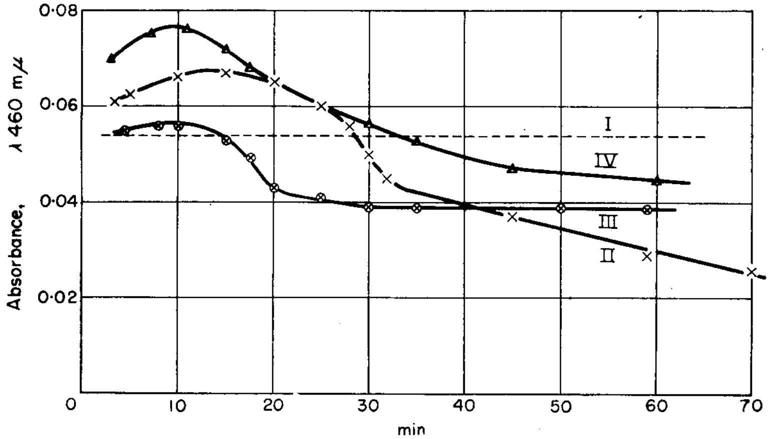

FIG. 6.—Effect of alkaline earths on absorption of the magnesium complex: (I) 1 ppm of Mg; (II) 1 ppm of Mg, 40 ppm of Ca; (III) 1 ppm of Mg, 30 ppm of Sr; (IV) 1 ppm of Mg, 40 ppm of Ca, 40 ppm of Sr.

(1) All three alkaline earths had to be present for the stabilising effect to be noticed (Fig. 7). If only two of the alkaline earths were present the behaviour was about the same as if only one was present.

(2) The buffer solution must be mixed with the reagent before addition. If it is added separately the solution becomes turbid.

(3) When barium and strontium are added the maximum amount of calcium that can be tolerated with certainty is 40 ppm. This can be held up by almost any combination of barium or strontium from 5 ppm of each to 5 ppm of barium with 40 ppm of strontium. With 1 ppm of magnesium an error of less than 10% was noted in most instances, if the reading was taken within 20 min from the time of mixing.

(4) Barium and strontium prevented calcium interference when the concentrations of magnesium or buffer are varied.

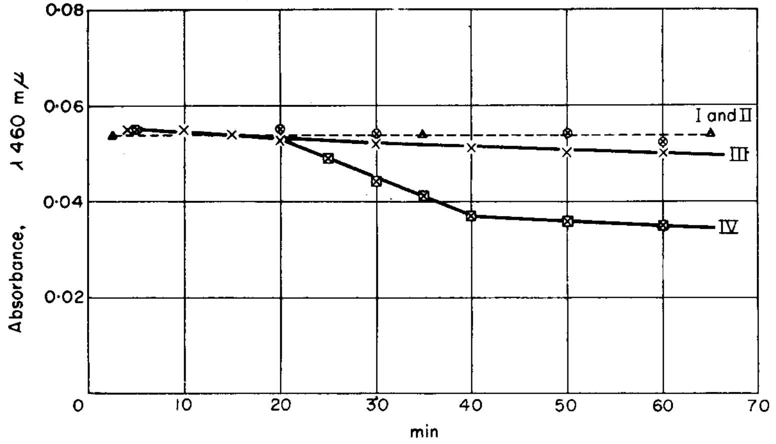

FIG. 7.—Effect of mixtures of alkaline earths on absorption of the magnesium complex: (I) 1 ppm of Mg; (II) 1 ppm of Mg, 40 ppm of Ca, 40 ppm of Sr, 40 ppm of Ba; (III) 1 ppm of Mg, 40 ppm of Ca, 20 ppm of Sr, 20 ppm of Ba; (IV) 1 ppm of Mg, 40 ppm of Ca, 10 ppm of Sr, 5 ppm of Ba.

(5) Each curve is not exactly reproducible. The shape of the curve is similar and the rate of drop in absorption is the same but the point at which the decline begins may vary.

From these results it was concluded that the effect was probably caused by supersaturation, although it could not be fully explained. In practice it was thought that calcium interference could be overcome by adding 20 ppm each of strontium and barium and reading after 15 min. It was found, however, in the analysis of solutions containing vaiious ions, that after the necessary separations had been made, calcium up to 40 ppm does not interfere.

ANALYSIS OF COMPLEX MIXTURES

All spectrophotometric methods for determining magnesium require the prior separation of other ions. Three ways were investigated:

(1) *Extraction with 8-quinolinol.* At pH 5 to 7, 8-quinolinol extracts many metals into chloroform or carbon tetrachloride.[16] It has been used as a means of removing interferences prior to a colorimetric determination of magnesium.[7] We found that results were a little low, probably because of incomplete removal of 8-quinolinol, and so the other two procedures are preferred.

(2) *Extraction with acetylacetone.* Between pH 3 and 7 acetylacetone extracts several ions into chloroform or carbon tetrachloride.[16] It has been used to remove interferences before making a magnesium determination.[17] The ions that are most effectively removed are those of aluminium, iron^{III}, copper, manganese, titanium, vanadium and uranium. If these ions and calcium are the only interferences procedure (2) was preferred because of its speed and ease.

(3) *Precipitation with ammonium hydroxide.* The classical double precipitation with ammonium hydroxide in the presence of ammonium chloride proved the most widely applicable method for the removal of interferences. Ammonia must be removed; this was done by evaporation to dryness with excess nitric acid.

ANALYSIS OF STANDARD SAMPLES

To test the efficiency of the method, two National Bureau of Standards samples of widely different composition were analysed.

NBS 102–*Silica Brick*

The principal interferences present and their percentages are SiO_2 (93·94), Al_2O_3 (1·96), CaO (2·29) and Fe_2O_3 (0·66). Other constituents present at the level of 0·01 to 0·3% are TiO_2, ZrO_2, MnO, Na_2O, K_2O and P_2O_5.

Procedure: Treat 1 g of the sample with hydrofluoric acid and a few drops of dilute sulphuric acid, and evaporate to dryness to remove the silica. Fuse the residue with sodium carbonate, take up the fusion mixture in dilute hydrochloric acid and add at least 10 ml of 70% perchloric acid. Evaporate the solution to dense fumes, then boil for 10 min. Add 30 to 40 ml of water, boil, filter and make up the filtrate to 100 ml. Take a 5-ml aliquot, adjust the pH to 3–4 with sodium bicarbonate and extract with 10 ml of acetylacetone solution (to remove the bulk of the iron), rejecting the organic layer. Adjust the pH to 7, extract twice more with acetylacetone, then with 10 ml of carbon tetrachloride. Make acid and extract twice more with carbon tetrachloride to remove the excess reagent. Transfer the aqueous layer to a small beaker, add a few drops of bromine water and evaporate to dryness. Take up the residue in water, adjust the pH to 9·0 to 9·5 with the aid of a pH meter and make up to 25 ml. Take a 2-ml aliquot, add 3 ml of NPAS solution, make up to 10 ml with water, mix, and read the absorbance at 450 mμ after 15 min. Obtain the magnesium value from a calibration curve prepared by applying the same procedure to standard magnesium solutions. Results with NBS 102 are shown in Table I.

TABLE I. ANALYSIS OF NBS 102
(MgO, 0·21%; range, 0·19–0·22%)

Sample No.	MgO, %
1	0·22[a]
2	0·215[b]
3	0·190[b]
4	0·207[c]
mean	0·208
stand. devn. =	0·0264 or 12·6%

[a] Av. of 4 determinations;
[b] Av. of 5 determinations;
[c] Av. of 6 determinations.

TABLE Ia. ANALYSIS OF VARIANCE FOR DATA FROM ANALYSIS OF NBS 102

Source of variation	Sum of squares	Deg. of freedom	Variance	Stand. devn.
Between samples	134	3	44·6	
Within samples	649	16	40·6	6·36
Total	783	19		

The table gives working units which are converted to % of MgO by adding 40 and multiplying by $4{\cdot}115 \times 10^{-3}$. Converting to % of MgO, stand. devn. = 0·0264 or 12·6%. Applying the F test,

$$\text{F ratio} = \frac{44{\cdot}6}{40{\cdot}6} = 1{\cdot}1$$

F values for 3 and 16 degrees of freedom for 5% and 1% are 3·24 and 5·29, respectively. Hence there is no reason to consider that the samples significantly differ.

NBS 87 *Aluminium–Silicon Alloy*

The main interferences in this sample are aluminium, silicon (6·21%), nickel (0·59%) and iron (0·46%). Others include copper, chromium, lead, manganese, tin, titanium and zinc. The high concentration of aluminium and the presence of tin and zinc made the precipitation procedure more satisfactory than the extraction technique.

Procedure: Weigh about 0·3 g of sample and dissolve as much as possible in dilute hydrochloric acid. Filter, keep the filtrate, burn off the filter paper and fuse the residue with sodium carbonate. Treat the fused mixture with perchloric acid as before and filter. Combine the filtrate with the first filtrate and make up to 100 ml. Take a 5-ml aliquot and treat with ammonium hydroxide according to Hillebrand *et al.*[18] Remove the ammonia by adding 10 to 15 ml of concentrated nitric acid and evaporating to dryness. The procedure from this point is the same as for NBS 102. The results with NBS 87 are shown in Table II.

TABLE II. ANALYSIS OF NBS 87
(Mg, 0·39%; range, 0·37–0·40%)

Sample No.	Mg, %
1	0·373
2	0·382
3	0·362
mean	0·372
stand. devn. = 0·0364 or 9·7%	

Each value is the average of 4 determinations.

TABLE IIa. ANALYSIS OF VARIANCE FOR DATA FROM ANALYSIS OF NBS 87

Source of variation	Sum of squares	Deg. of freedom	Variance	Stand. devn.
Between samples	919	2	459·5	21·43
Within samples	11937	9	1324	36·4
Total	12856	11		

The table gives working units which are converted to % of Mg by adding 300 and multiplying by 1000. Converting to % of Mg, stand. devn. = 0·0364 or 9·7%. Applying the F test, F ratio = $\frac{1324}{459 \cdot 5} = 2 \cdot 88$.

F values for 9 and 2 degrees of freedom at 5% and 1% levels are 4·26 and 8·2, respectively. Therefore there is no reason to consider that the samples significantly differ.

Precision

To obtain the precision of the method in pure magnesium solutions, the same amount of magnesium was determined 11 times. The average absorption was 0·125 and the standard deviation 0·00094 or 0·7%. This precision is not obtained when a complex mixture is analysed. The data for the precision of two such analyses are given in Tables Ia and IIa. The values were obtained by following the statistical procedures recommended by Davies.[19] It can be seen that the precision for complex mixtures is about 10%. The difference between NBS 102 and NBS 87 probably reflects the longer experimental procedure, rather than a marked difference between the extraction and precipitation method of separation.

Zusammenfassung—5-(3-nitrophenylazo)salizylsäure (als Natriumsalz) reagiert be pH 10·5 nahezu spezifisch mit Magnesium unter Bildung eines gelb gefärbten Chelates. Die Lösung zeigt ein Absorptionsmaximum be 450 mμ. Die Empfindlichkeit der Reaktion ist 0·01 μg Magnesium per cm^2 für log $I_0/I = 0 \cdot 001$. Die optimalen Bedingungen für die Reaktion wurden ermittelt. Die Ausarbeitung einer spektrophotometrischen Methode zur Bestimmung von Magnesium erfolgte auf Grund der Studien über Einfluss von pH der Lösung, Verhältnis Magnesium zu Reagens, Gültigkeit von Beer's Gesetz und Geschwindikeit der Farbentwicklung. Die Methode wurde mit Erfolg auf die Bestimmung von Magnesium in Ziegeln und Silizium-Aluminum Legierung angewendet.

Résumé—L'acide 5-(3-nitrophénylazo)salicylique (sel de sodium) réagit presque spécifiquement avec les ions magnésium (à pH 10,5) pour donner un chelate de couleur jaune. La solution a une absorption maximale à 450 $\mathrm{m}\mu$. La sensibilité de la réaction est 0,01 μg de magnésium par cm^2 pour $\log I_0/I = 0{,}001$. Les conditions les meilleures de la réaction ont été établies.

La mise au point de la méthode spectrophotométrique de dosage du magnésium nécessite une étude de l'action du pH, du rapport réactif/magnésium, de la stabilité photométrique du complexe, de la vitesse de formation de la couleur; il faut, de plus, savoir si le complexe suit la loi de Beer.

La méthode a été appliquée avec succès au dosage du magnésium dans la brique de silice et dans l'alliage silicium-aluminium.

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THE COULOMETRY AND POLAROGRAPHY OF IRIDIUM^{IV}

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Summary—The coulometric and polarographic behaviour of iridium^{IV} has been investigated. In a 0·2*M* hydrochloric acid electrolyte, at potentials negative enough to prevent the oxidation of the mercury, the iridium gives a diffusion current plateau suitable for polarographic determinations. Electrolysis at a controlled electrode potential shows that the reduction requires one electron per mole, and has been used for the coulometric determination of 3- to 17-mg amounts of iridium. The behaviour of iridium in other electrolytes has also been investigated.

INTRODUCTION

A SURVEY of the literature has revealed no polarographic procedures suitable for the determination of iridium. A recent critical review[1] has discussed the titrimetric methods that have been recorded for iridium, most of which involve the titration of the strongly oxidising iridium^{IV} in acid solution with reducing agents.

In most cases these reductions proceeded smoothly and rapidly at room temperature. The present study shows that the corresponding reduction of iridium can be carried out at a mercury or platinum cathode controlled at a suitable potential, and can be used for a coulometric or polarographic determination of iridium.

EXPERIMENTAL

Apparatus

The controlled-potential coulometric titrations were carried out using an apparatus patterned on that of Kelley, Jones and Fisher.[2] The current integrator was an operational amplifier with capacitance feedback, and the titration output was read and followed on a Brown Instrument 10-mV strip-chart recorder. The titration instrument was calibrated using a 100-ohm standard resistance in place of the cell. The calibration current was calculated from the potential drop across the standard resistance as measured with a potentiometer and standard cell. The output was 0·530 coulombs per mV with a 50-K ohm input resistor and 0·265 coulombs per mV with a 100-K ohm input resistor.

Diaphragm-type cells with mechanical stirring were used for all electrolyses. For titrations employing a platinum electrode (oxidations and reductions), the cell was a 100-ml tall-form beaker, and the electrode was a cylindrical cage, 2·5 cm in diameter, consisting of 7 loops of 1-mm wide platinum foil. The inner compartment, a chamber 1·5 cm in diameter, was separated from the outer cell by an ultrafine fritted-glass disc.

For controlled potential reductions with a mercury cathode an H-type cell was used. The cathode compartment had a volume of 100 ml and the electrode consisted of 20 ml of mercury with a surface area of 16 cm^2. The mercury was introduced into the cell by a bottom stopcock and levelling bulb, but only after de-aeration of the electrolyte was complete. The two compartments of the cell were separated by a coarse fritted-glass disc backed by an agar-potassium chloride gel.

The reference electrode was a Beckman Instruments 5″ external saturated calomel electrode with a fibre-type junction. For the titrations in solutions containing perchlorate, an intermediate bridge containing 1*M* hydrochloric acid was used with the reference electrode. A silver-silver chloride working electrode in 1*M* hydrochloric acid was used in the second compartment in all titrations. Prepurified nitrogen (less than 20 ppm of oxygen) was used to displace the oxygen from the electrolysis solutions.

Polarograms were recorded on a Leeds and Northrup Type E Electrochemograph using a conventional H-type cell with a saturated calomel reference electrode. Absorption spectra were recorded on a Bausch and Lomb Spectronic 505 recording instrument using matched 1-cm quartz cells.

All potentials, in V, are relative to the saturated calomel electrode, unless otherwise noted.

Standard iridium solution

The stock solution was prepared by dissolving 1·90 g of sodium chloroiridate (Johnson, Matthey and Co.) in 2 litres of 0·1*M* hydrochloric acid. The solution was standardised gravimetrically by precipitation of the hydrous oxide using the method of Gilchrist.[3] Three 50-ml aliquots of the solution gave, on ignition in hydrogen, 16·9, 16·9 and 17·2 mg of iridium. Subsequent coulometric titrations of 10-ml aliquots of the solution showed no significant trend over a period of 3 months, indicating that the iridium^{IV} was stable. Other 10-ml aliquots of the solution were added to 80 ml of 0·2*M* hydrochloric acid, heated to 80°, and treated with chlorine for 30 min. The excess chlorine was then removed by boiling, the solution was cooled, and the iridium was determined by coulometric titration. The treatment with chlorine produced no change in the results of the coulometric titration, indicating that the standard solution contained insignificant amounts of iridium^{III}.

Studies in hydrochloric acid

Polarography of iridium^{IV} *in* 0·2M *hydrochloric acid:* In a 0·2*M* hydrochloric acid supporting electrolyte, iridium^{IV} gives a well defined diffusion current plateau at potentials negative enough to prevent the oxidation of the mercury. The diffusion current was found to be proportional to the concentration of iridium^{IV}, and, at fixed concentration, to the square root of the height of the mercury column of the dropping electrode, indicating a diffusion controlled process (Table I).

TABLE I

	C_{Ir}^{IV}, *mM*	i_d*, *μ amp*	i_d*/C	i_d*/C$h^{1/2}$
h 36·0 cm	0·442	1·15	2·60	
m 1·514 mg/sec	0·884	2·29	2·59	
t* 5·34 sec	1·327	3·47	2·61	
		mean	2·60	0·43
h 49·0 cm	0·442	1·33	3·01	
m 2·087 mg/sec	0·884	2·67	3·02	
t* 3·82 sec	1·327	4·03	3·04	
		mean	3·02	0·43

* i_d and t measured at −0·20 V; 25°

Controlled potential electrolysis: Controlled potential reductions of the iridium^{IV} at either a mercury cathode at 0 V or a platinum cathode at 0 or 0·40 V in the 0·2*M* hydrochloric acid electrolyte gave results consistent with a 1 faraday per mole reduction. The potential of an iridium solution after passage of 50% of the total quantity of electricity necessary for the reduction was measured with a platinum indicator electrode and found to be +0·81 V at 25°. This permits the assignment of the formal potential to the couple in 0·2*M* hydrochloric acid:

$$IrCl_6^{2-} + e \rightleftharpoons IrCl_6^{3-}, \quad E^\circ = +1{\cdot}05 \text{ V } \textit{vs.} \text{ N.H.E.}$$

Quantities of iridium from 3 to 16 mg have been determined by a controlled potential reduction based on an equivalent weight of 192·2 for the iridium (Table II). The titrations were carried out after a pre-electrolysis of the supporting electrolyte. An 80-ml portion of the 0·2*M* hydrochloric acid electrolyte was introduced into the cell, de-aerated, and then reduced at the potential to be used in the subsequent determination. The electrolysis was continued until a negligible residual current was obtained (0·01 mA), then the circuit was interrupted, in the case of mercury the cathode was withdrawn from the cell, and the sample aliquot was added. The titration was not initiated until sufficient time had elapsed for the displacement by the nitrogen of the dissolved oxygen introduced with the sample. Electrolysis for 60 min was generally sufficient to give a quantitative reduction. The current decreased in an exponential fashion to a negligible residue (0·01–0·03 mA).

TABLE II

Reduction	Ir taken, *mg*	Ir found, *mg*
Pt cathode, 0 V	17·0	16·72, 16·66
	8·5	8·34, 8·39
	3·40	3·26, 3·28, 3·32[a]
		3·32, 3·34[a] 3·35
		3·32[b], 3·35[b]
	9·15[c]	9·02, 9·06
	10·3[d]	9·82, 9·85
Pt cathode, 0·40 V	3·40	3·30, 3·36
Hg cathode, 0 V	8·5	8·21, 8·26
	3·40	3·32, 3·31
		3·31[b], 3·31[b]

[a] Ir solution treated with Cl_2 before determination.

[b] Ir reduced at a Pt cathode, 0 V, then reoxidised with Cl_2 before determination.

[c] $(NH_4)_2IrCl_6$ solution standardised against 2-mercaptobenzothiazole[5] (G.G.T.)

[d] Na_2IrCl_6 solution standardised by hydrolytic precipitation (H.I.R.Z.)

The reduced iridium solution could be quantitatively oxidised back to iridium^{IV} by bubbling chlorine through the hot acid solution for 60 min. The excess chlorine could then be removed by gentle boiling for 30 min and the iridium determined by coulometric titration. Boiling of the solution for up to 120 min, maintaining the volume by the addition of water, was found to have no effect on the results of the subsequent titration.

The mean value for the twenty titrations of aliquots of the standard iridium solution was 0·332 mg of iridium per ml, with an average deviation of 0·002 mg. The result differs from the mean value of 0·340 mg per ml obtained by hydrolytic precipitation, but it has been said that this method gives high results.[4]

Attempts to oxidise the reduced iridium solutions at a platinum anode controlled at +1·0 V gave large and steady residual currents (0·3 to 0·5 mA). Subsequent coulometric reduction of these solutions, after boiling to remove any chlorine, gave high results for the iridium.

Studies in perchloric acid

Aliquots of the standard iridium solution were fumed with 10-ml portions of 72% perchloric acid for 30 min, washed down, and again fumed for a further 30 min before dilution to 100 ml. Polarography of the resulting purple solutions gave well defined diffusion current plateaux at potentials negative enough to prevent the oxidation of the mercury. The diffusion current was, in all cases, considerably greater than that in the 0·2*M* hydrochloric acid electrolyte under equivalent conditions, but consistent results could not be obtained. Controlled potential coulometric reductions at a platinum cathode at 0 V were carried out on iridium samples fumed in this fashion. The electrolyses proceeded smoothly with an exponential decay of the current to a small residual value (0·01 to 0·03 mA), but values from 1·39 to 1·76 faradays per mole were obtained in the series of ten reductions.

It would appear that the fuming with perchloric acid gave a partial and variable oxidation of the iridium^{IV} to a higher state. This is in agreement with the results obtained by McBryde and Cluett[6] for the potentiometric titration with iron^{II} or titanium^{III} of iridium fumed in perchloric acid.

Studies in sulphuric acid

Aliquots of the standard iridium solution were fumed with 10-ml portions of concentrated sulphuric acid for 30 min, washed down, and again fumed for a further 30 min before dilution to 100 ml. Polarography of the resulting colourless solutions gave no reduction wave before the discharge of the supporting electrolyte at a potential of −0·75 V. Attempts to oxidise these fumed iridium solutions at a platinum anode at potentials up to +1·0 V gave only the anode reaction corresponding to that of the electrolyte without iridium.

No conclusion can be drawn respecting the oxidation state of the colourless complex in the fumed solution.

Studies in other electrolytes

The polarography of iridium^{IV} was investigated in an electrolyte 1M in sodium hydroxide and in an electrolyte 1M in ethylenediaminetetra-acetic acid and 1M in sodium hydroxide. No reduction waves were obtained, in agreement with the results previously reported by Willis[7] for ammonia, cyanide, ethylenediamine, pyridine and thiocyanate electrolytes. This indicates that in the presence of alkali or other complexing agents the iridium^{IV} either forms a complex that is not reducible at the dropping mercury electrode or the iridium^{IV} is unstable and has undergone spontaneous reduction.

An examination of the absorption spectra gives some indication of the nature of the reaction (Fig. 1). If an iridium^{III} solution prepared by a controlled potential reduction in 0·2M hydrochloric acid is made 0·1M in excess sodium hydroxide, a spectrum with a peak at 317 mμ immediately develops and is stable on long standing. If an iridium^{IV} solution in 0·2M hydrochloric acid is similarly made 0·1M in excess sodium hydroxide, the solution immediately turns colourless and then, over a period of 48 hr in the dark, slowly develops a spectrum identical with that of the iridium^{III} solution. The reaction is catalysed by sunlight. The disappearance of the iridium^{IV} can be followed by reacidification of aliquots of the solution at intervals of time. Reacidification of the final solutions with hydrochloric acid gave, in both cases, the colourless solution characteristic of iridium^{III}, and subsequent oxidation with chlorine restored the brown colour of iridium^{IV}.

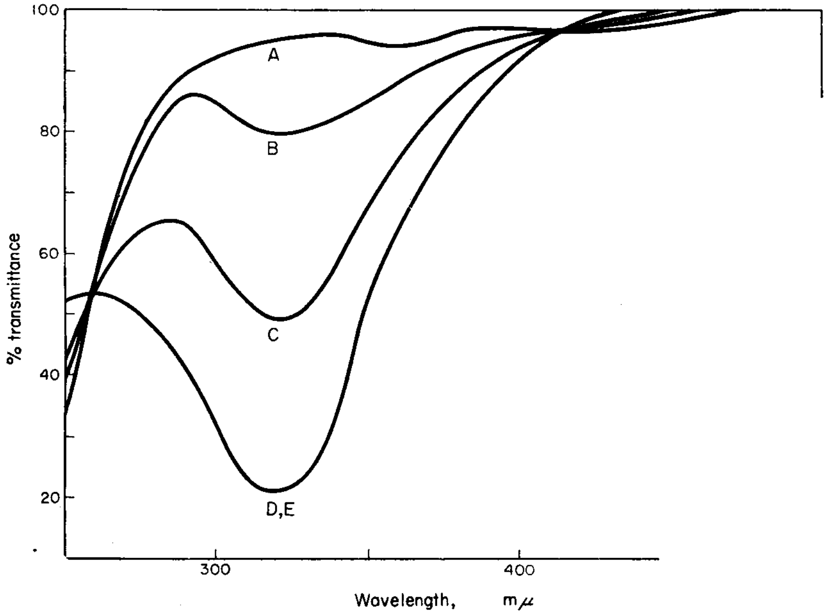

FIG. 1.—Spectrum of 0·30 mM iridium solutions in 0·1M excess sodium hydroxide:
Ir^{IV}: A, on mixing; B, 2 hr; C, 8 hr; D, 48 hr standing
Ir^{III}: E, on mixing.

A similar reaction was found to take place in the 1M ethylenediaminetetra-acetic acid plus 1M sodium hydroxide electrolyte, except that the absorption peak was shifted to 315 mμ. This peak is the basis of the spectrophotometric determination of iridium^{IV} proposed by MacNevin and Kriege.[8]

It would appear that the iridium^{IV} is reduced to iridium^{III} in the basic solutions. However, the immediate disappearance of the polarographic wave in basic solution contrasts with the slow appearance of the iridium^{III} spectrum in the air-saturated solutions. It would appear that the iridium^{IV} complex in basic solution does not react at the dropping mercury electrode at any appreciable rate.

DISCUSSION

Polarography in 0·2M hydrochloric acid provides a means for the relative assay of pure iridium^{IV} solutions. The method must be standardised against solutions of known iridium content. Coulometry in the 0·2M hydrochloric acid electrolyte provides a means for the absolute assay of a pure iridium^{IV} solution. The method is standardised by reference to a standard cell and a standard resistance.

Application of these methods to the determination of iridium in a general scheme of analysis would depend greatly on the nature of the sample. Reference to the standard potentials of the appropriate couples,[9] indicates that gold^{III}, palladium^{II}, platinum^{IV} and rhodium^{III}, amongst others, would be expected to interfere. The degree of complexity of the equilibria of these metals in mineral acid solution is such however, that specific solution preparations might give no interference.

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Zusammenfassung—Das coulometrische und polarographische Verhalten von Iridium(IV) wurden untersucht. In 0,2 m Salzsäure als Elektrolyt ist das Potential genügend negativ um eine Oxydation von Quecksilber auszuschalten. Iridium zeigt ein Plateau in der Strom-Spannungskurve, welches geeignet für polarographische Bestimmungen ist. Elektrolyse mit kontrolliertem potential zeigt, dass ein Elektron zur Reduktion nötig ist. Die coulometrische Bestimmung von 3–17 mg Iridium wurde elfolgreich druchgeführt. Das Verhalten von Iridium in anderen Elektrolyten wurde ebenfalls studiert.

Résumé—L'auteur a étudié le comportement coulométrique et polarographique de l'iridium(IV). En milieu acide chlorhydrique 0,2*M*, à des potentiels suffisamment négatifs pour empêcher l'oxydation du mercure, l'iridium donne une vague de diffusion convenable pour des dosages polarographiques. L'électrolyse à potentiel contrôlé montre que la réduction nécessite un électron par mole; elle a été utilisée pour le dosage coulométrique de 3 à 17 mg d'iridium.

Le comportement de l'iridium dans d'autres électrolytes a aussi été étudié.

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MIXED CHEMILUMINESCENT INDICATORS

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Summary—A 1 : 1 molar mixture of luminol and fluorescein in the presence of hydrogen peroxide has been shown to be a sensitive and reversible chemiluminescent indicator for acid-base titrations. The role played by the fluorescein and luminol is discussed.

THE use of chemiluminescent indicators in titrimetric analysis has been thoroughly investigated by Erdey and coworkers and the results have been summarised.[1]

For acid-base titrations, the indicators lucigenin, luminol and lophine have been used. Lucigenin is the most satisfactory since no catalysts are required and the indicating reaction is reversible. The intensity of chemiluminescence is less than that obtained from catalysed luminol solutions but luminol is irreversibly destroyed in alkaline solution and accordingly is only recommended for the titration of acids with bases.

We have observed that the intensity of lucigenin chemiluminescence can be markedly increased by adding fluorescein. A similar increase was observed on mixing fluorescein and luminol and, as described in this paper, this mixture has proved to be useful as a reversible indicator for acid-base titrations. The effect of fluorescein is discussed in this paper and an indicator reaction mechanism proposed. Further studies are being made of the behaviour of other materials which fluoresce strongly.

EXPERIMENTAL

Effect of fluorescein on chemiluminescence

Either 1 ml of 0·2% lucigenin solution or 1 ml of 0·1% luminol solution was added to 10-ml aliquots of 0·01*N* sodium hydroxide solution containing 1 ml of 6% H_2O_2, and these alkaline peroxide solutions were heated to *ca.* 60°. To each aliquot, a volume (0–5 ml) of 0·25% sodium fluoresceinate was added.

In the absence of fluorescein, the heated alkaline solutions emitted greenish-white light on the addition of lucigenin and pale blue chemiluminescence on the addition of luminol. On the inclusion of increasing amounts of fluorescein in the solutions, the emitted light increased in intensity and finally had the characteristic bright green colour observed during the fluorescence of fluorescein. The intensity increased with increasing concentration of fluorescein up to the point where the fluorescein concentration was approximately double the concentration of luminol present. With higher concentrations of fluorescein the intensity decreased from this maximum because of self-absorption by the dye molecules.

When solutions containing luminol were cooled the colour faded rapidly, the rate of fading decreasing with increasing concentration of fluorescein present.

In another series, the fluorescein content was kept constant and the luminol content varied. In these tests, a marked increase in chemiluminescence intensity occurred on increasing the amount of luminol present up to approximately half the percentage composition of fluorescein present, but no significant increase resulted from adding larger volumes.

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The most suitable mixture for use as an indicator was thus found to be a combination of equal volumes of 0·1% luminol and 0·25% fluorescein, *i.e.* about a 1:1 molar mixture. Decreasing volumes of this mixed indicator solution were then added to hot alkaline peroxide solutions to determine the sensitivity of the indicator. In the presence of 1 ml of indicator per 20 ml of solution, chemiluminescence of moderate intensity was retained even on cooling. Provided the alkaline solutions were maintained hot, a pale chemiluminescence was obtained in the presence of 0·01 ml of indicator per 20 ml of solution and the light was just discernible if this amount of indicator was halved.

Titrations using fluorescein-luminol mixed indicator

The mixed indicator solution was prepared by dissolving 0·25 g of fluorescein and 0·1 g of luminol in 10 ml of 0·1*N* sodium hydroxide solution and diluting to 100 ml.

One ml of 6% H_2O_2 and 1 ml of indicator solution were added to 20·00-ml aliquots of standard hydrochloric acid solutions. The solutions were heated to 60° and titrated in the dark with standard sodium hydroxide solution to the appearance of permanent chemiluminescence. Measurements with a pH meter showed that this chemiluminescence appeared at a pH of 8·9. Excess base was then added, and the solution back-titrated with acid to the disappearance of light. In another series, the starting point was 20·00-ml aliquots of standard sodium hydroxide solution. The results are summarised in Table I.

TABLE I.—ACID-BASE TITRATIONS

Titrant	Mean of ten titrations, *ml*	Precision (standard deviation) *ml*	Precision (standard deviation) %	Deviation from phenolphthalein, %
1*N* NaOH	19·97	±0·04	±0·20	0·15
0·1*N* NaOH	20·05	±0·07	±0·35	0·20
0·01*N* NaOH	20·90	±0·17	±0·85	0·50
1*N* HCl	19·97	±0·04	±0·20	0·15
0·1*N* HCl	19·83*	±0·06	±0·30	0·40
0·01*N* HCl	18·11*	±0·26	±1·45	1·00

* Low values because of the presence of 5×10^{-4} moles of Na_2CO_3 per litre of NaOH.

Since the peroxide solution had a slight acidity and the indicator a slight alkalinity, it was necessary to determine a reagent blank by taking 5 ml of indicator and 5 ml of 6% H_2O_2 in 20 ml of hot water and titrating with standard base (preferably 0·01*N*) to the appearance of light. In the above titrations, the indicator plus peroxide blank amounted to 0·40 ml of 0·01*N* sodium hydroxide solution and this correction was applied to all direct titration values.

To test the suitability of the indicator for micro-titrations 5-ml aliquots of 0·1*N* solutions of acetic, citric, oxalic and tartaric acids were titrated with 0·1*N* sodium hydroxide solution using 1 ml of 6% H_2O_2 and 1 ml of mixed indicator per aliquot. The titrations were repeated using phenolphthalein as indicator and the results are compared in Table II. It can be seen from this table and from the

TABLE II.—TITRATION OF 5·00 ml OF 0·1*N* WEAK ACID SOLUTIONS WITH 0·1*N* SODIUM HYDROXIDE SOLUTION

Acid	Mean of six titrations: Phenolphthalein, *ml*	Mean of six titrations: Luminol-fluorescein, *ml*	Deviation between the two results, %
Acetic	4·97	4·99	0·4
Citric	4·95	5·24*	6·0
Oxalic	4·99	4·97	0·4
Tartaric	4·98	4·97	0·2

* Indistinct end-point; chemiluminescence masked.

deviations noted in Table I that, with the exception of the titration of citric acid, the mixed indicator gave similar titration values to those obtained using phenolphthalein indicator.

The indicator proved to be completely reversible provided that the titrations were commenced at *ca.* 60°. Similar titres were obtained in direct titrations and in back titrations and the precision values quoted in Table I are derived from the values obtained in both ways. It was possible to titrate a solution back and forth at least six times without any further addition of indicator.

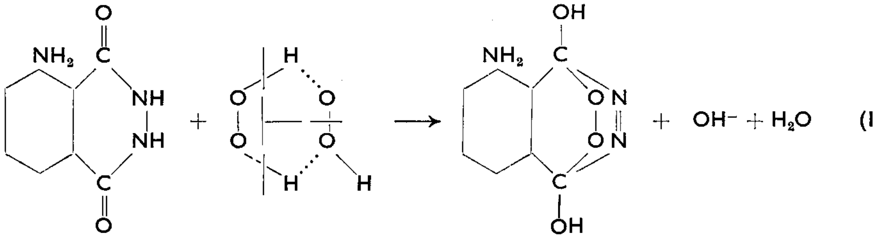
Some warning of the approach of the equivalence point was obtained with this indicator. In titrations with alkali, the duration of the flashes of light obtained on the addition of drops of titrant increased near the equivalence point. When titrating with acid solutions, there was a dimming of the chemiluminescence before complete extinction. Greater sensitivity was obtained by shaking the solutions vigorously at this stage of the titration.

DISCUSSION

In the original study of the use of luminol as an acid-base indicator, Kenny and Kurtz[2] used 40 mg of luminol and 30 mg of haemin catalyst per titration and the indicator reaction was irreversible. In the present study only 1 mg of luminol and 2·5 mg of fluoroscein were used per titration, the indicator reaction proved reversible, and the precision obtained was equivalent to that recorded in earlier studies. A similar saving in indicator material may be obtained using lucigenin since the presence of fluorescein greatly enhances the intensity of the emitted light.

The role played by fluorescein in these mixed indicators requires some explanation. Fluorescein, eosin and rhodamine chemiluminesce with a colour tone resembling fluorescence when oxidised with hydrogen peroxide in sodium hydroxide solution, the intensity of the chemiluminescence increasing with temperature and with increasing concentrations of alkali, dye and hydrogen peroxide.[3] With the concentrations of reactants used in this study, only very weak emissions are observed unless luminol is added. If the luminol is destroyed by adding other catalysts, such as haemin or heavy metal ions, there is a marked increase in brilliance as the luminol reacts with these catalysts, then the solution reverts to the pale luminescence of the fluorescein or eosin present. The intensity can be restored by adding further luminol. It can, therefore, be suggested that luminol is acting as a catalyst for the chemiluminescent reaction of xanthene dyes.

In the mechanisms proposed to explain the chemiluminescence of lucigenin and luminol, the primary step is envisaged as the formation of a trans-annular peroxide.[1] With hydrogen peroxide as the oxidising agent, the reaction with luminol can be written as follows:



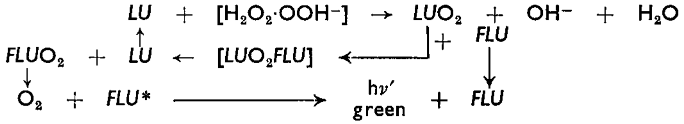
(I)

Hydrogen peroxide can exist in several forms in aqueous solution depending on the pH of the solution. At pH < 12, the hydrogen peroxide is present mainly as molecular H_2O_2. On increasing the pH, perhydroxyl ions are formed in the solution and react with excess H_2O_2 to give the ion $H_2O_2{\cdot}OOH^-$, which reaches a maximum concentration at pH 12.[4,5] Above pH 12 the concentration of perhydroxyl ions increases and at pH 14 the species present is mainly the perhydroxyl ion. In the mixed indicator, a maximum emission of light was observed at pH *ca.* 12 so that the preferred species of hydrogen peroxide for the oxidation must be $H_2O_2{\cdot}OOH^-$ as shown in equation (1).

The reaction of hydrogen peroxide with lucigenin, eosin, fluorescein, *etc.* can be written in an analogous manner.

The formation of the trans-annular peroxide compound facilitates singlet-triplet conversion within the molecule through the triplet state or magnetic field associated with the oxygen. If the peroxide now be decomposed, the remaining molecule is left in an excited, unstable triplet state which reverts to the singlet state with the emission of light.

The luminol can catalyse the chemiluminescence of fluorescein by facilitating the formation of fluorescein peroxide through formation of a transitional complex and oxygen transfer. Using *LU* and *FLU* as abbreviations for luminol and fluorescein, respectively, the light producing mechanism can be summarised as follows:

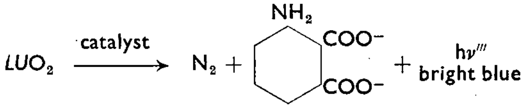


(2)

In the absence of fluorescein or catalysts, the LUO_2 can be decomposed by heat, but this reaction is slow:

$$LUO_2 \xrightarrow{\text{heat}} O_2 + LU^* \longrightarrow LU + \underset{\text{deep blue}}{h\nu''} \tag{3}$$

In the presence of catalysts such as haemin and heavy metal ions, luminol is irreversibly oxidised by a different mechanism and yields the following products:[1]



(4)

The role of luminol in reaction (2) is similar to the role played by sensitisers in the photo-oxidation of organic compounds, and it is interesting to note that eosin has been widely used as a sensitiser for the preparation of the trans-annular peroxides of a number of steroids and linear polyacene aromatic hydrocarbons.[6] In these preparations, the role of the sensitiser is that of a carrier of reactive oxygen to the substrate, thus allowing the oxidation to proceed by a considerably lowered barrier.

It is possible to suggest an alternative mechanism in which fluorescein can be regarded as a catalyst for the decomposition of the luminol peroxide, resulting in an increased yield of the deep blue light observed on thermal decomposition [*cf.* equation (3)]. These radiations can then be presumed to activate the fluorescein and result in a green fluorescence. This mechanism was not supported by experimental evidence, for no green fluorescence was observed when luminol, chemiluminescing from thermal decomposition, was separated by a glass wall from alkaline fluorescein solution, but mixing of the two solutions yielded bright green light immediately. Collision of the two molecules must therefore be an integral part of the mechanism.

A similar set of equations can be written to explain the behaviour of lucigenin–fluorescein mixtures.

On the basis of the proposed mechanism, a number of fluorescent materials could be sensitised. In this way it should be possible to develop a series of mixed chemiluminescent indicators which would be useful for a variety of titrations.

Acknowledgements—Two of us (L. E. and W. F. P.) wish to acknowledge Research Fellowships from the Queen's University, Belfast, which made participation in this project possible.

Zusammenfassung—Eine 1:1 (Molbasis) Mischung von Luminol und Fluorescein ist in Gegenwart von Wasserstoffperoxyd ein empfindlicher und reversibler Chemiluminiszenzindicator für Säure-Basentitrationen. Die Wirkung der beiden Substanzen wird diskutiert.

Résumé—Les auteurs ont montré qu'un mélange mole à mole de luminol et de fluorescéine était un indicateur chimioluminescent sensible et réversible pour les titrages acide-base. Le röle joué par la fluorescéine et le luminol est discuté.

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IMPROVED PYROGALLOL DETERMINATION OF NIOBIUM BASED UPON EXTRACTION OF A QUATERNARY AMMONIUM ION COMPLEX

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Summary—The optical absorbance produced by mixing niobium^{V} with pyrogallol in a slightly alkaline solution is increased approximately 60% by the presence of a long-chain quaternary ammonium compound. In addition, the interferences from molybdenum^{VI}, tungsten^{VI} and chromium^{VI} can be virtually eliminated and that from vanadium^{V} halved by an extraction of the niobium complex with ethyl acetate. Tantalum accompanies niobium but, by selection of the wavelength, interference from moderate amounts can be minimised. Interference by titanium is very serious but somewhat less than in the original procedure of Hunt and Wells.

INTRODUCTION

As the result of a study on the enrichment and eventual separation of niobium and tantalum by foam fractionation, a reliable and simple method was required to determine each of these elements in the presence of the long-chain quaternary ammonium salt used as the foam-producing agent. Among the available methods for niobium, one using pyrogallol[23] was preferred to the others, mainly because of the possibility of applying it to dilute aqueous solution without further preparation and because the same reagent could be used, under different conditions, for tantalum. In contrast, the peroxy method requires one to work with fairly concentrated sulphuric acid, and its sensitivity is rather poor.[4,6,14,22,29,30] The thiocyanate approach is still subject to a series of interferences and, in addition, uses a very volatile solvent (ethyl ether) in its most sensitive modification.[2,3,11,13,31] Finally, the hydroquinone procedure is quite sensitive to temperature.[8,13,19]

Successive modifications and improvements of the pyrogallol method have been reported and reviewed in detail by different authors.[5,7,12,32,33] The Hunt and Wells technique[12] was chosen among them as a basis for our study because of its relative simplicity.

The present study shows that the sensitivity of the Hunt and Wells procedure[12] is nearly doubled in the presence of a long-chain tetra-alkylammonium salt, and that the specificity of the procedure can be markedly improved by extraction with ethyl acetate.

EXPERIMENTAL

Reagents

Salt mixture: A solution to simulate a typical one in which niobium might be found after fusions of an ore or alloy was made up to contain sulphate, oxalate and citrate. Citrate was present as well as oxalate to form soluble complexes and also because the oxalate was much less soluble than citrate. One litre of solution containing 62·5 g of $Na_2SO_4\cdot 10\ H_2O$ and 62·5 g of $(NH_4)_2HC_6H_5O_7$ was mixed with an equal volume of 4% ammonium oxalate solution.

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Test solutions: Stock solutions ($1 \times 10^{-2}M$) of niobium^{V} and tantalum^{V} were prepared by dissolving an appropriate amount of the metal in a platinum dish using 10 ml of 48% hydrofluoric acid plus a few drops of concentrated nitric acid. After evaporation on a steam bath to about 5 ml, the solution was made up to 1 litre. The diluent for niobium was 4% ammonium oxalate solution; that for tantalum was the salt mixture.

Titanium^{IV} was prepared in the same way as the tantalum except that TiO_2 was used as the starting material. The $0{\cdot}5M$ solutions of tungsten^{VI}, molybdenum^{VI}, vanadium^{V}, and phosphate were prepared by dissolving $Na_2WO_4{\cdot}2\,H_2O$, $Na_2MoO_4{\cdot}2\,H_2O$, $Na_3VO_4{\cdot}16\,H_2O$, and $Na_2HPO_4{\cdot}7\,H_2O$ in distilled water. The vanadate solution had to be filtered to remove a slight turbidity; further dilutions, $5{\cdot}0 \times 10^{-2}M$ and $5{\cdot}0 \times 10^{-3}M$, were prepared with 4% ammonium oxalate solution, except for vanadate and tungstate which had to be diluted with water.

The $0{\cdot}5M$ solutions of chromium^{VI} and fluoride were prepared from $Na_2CrO_4{\cdot}4\,H_2O$ and NaF using 4% ammonium oxalate solution as solvent. Another fluoride solution was prepared in water.

Sodium bisulphate solution, 9% aqueous: This was substituted for the potassium salt in the Hunt and Wells procedure[12] to minimise the potassium content.

Ethoquad 18/25 (*polyethoxy-*15*-stearyl-methylammonium chloride*) *solution,* $0{\cdot}001M$*:* Prepared by diluting 1 g to 1 litre with salt mixture (or with 4% ammonium oxalate solution or with water in certain cases).

Pyrogallol reagent: Immediately before use dissolve 4 g of pyrogallol in 120 ml of 10% anhydrous sodium sulphite and dilute to 200 ml.

Wash solution: Ethyl acetate extracts were washed with portions of a mixture prepared from 80 ml of 10% sodium sulphite plus 80 ml of $0{\cdot}001M$ Ethoquad (in salt solution) diluted to 200 ml.

Apparatus

Spectrophotometric measurements were made with a Beckman DU instrument equipped with silica cells. pH measurements were made with a glass electrode connected to a Beckman Zeromatic pH meter.

Procedure

The adopted technique ensures that the concentrations of reagents in the aqueous sample are 2·5% citrate, 2·5 sulphate, 2·4% sulphite, 0·48% oxalate, $4{\cdot}0 \times 10^{-4}M$ Ethoquad, and 0·8% pyrogallol The pH is 7·5 ± 0·1. These conditions are attained by adding to a sample 20 ml of Ethoquad reagent (in salt mixture), 5 ml of $1M$ sodium hydroxide, 20 ml of pyrogallol reagent, and diluting to 50 ml with water.

The absorbance of the above mixture can be measured at 410 mμ against a similar blank to determine niobium with little interference from tantalum, but extraction into ethyl acetate is preferred for better selectivity even though the sensitivity is slightly less. Extraction of a 25-ml aliquot of sample is performed in a 125-ml separatory funnel of the Squibb type. Successively, 10-, 5- and 5-ml portions of ethyl acetate are shaken vigorously for 2 min each. The collected extracts are then washed three times with 5-ml portions of wash solution and, finally, filtered into a 25-ml calibrated flask through about 8 g of anhydrous sodium sulphite. The latter serves to dry the extract and simultaneously prevent its oxidation. The extract is diluted to volume and the absorbance at 410 mμ measured against an ethyl acetate blank.

RESULTS

Preliminary work

Niobium and pyrogallol are reported[16] to form a 1:1 complex in aqueous solution. However, it has been confirmed that a large excess of pyrogallol is required to attain a maximum absorbance, a situation similar to that reported for the titanium complex.[28] Under Hunt and Wells's conditions[12] the presence of Ethoquad enhanced the absorption without shifting the peak at 358 mμ (Fig. 1). The absorption value was independent of the order of mixing the reagents. By adding increasing amounts of Ethoquad to a solution containing $4{\cdot}0 \times 10^{-5}M$ niobium and 0·8% pyrogallol, a combining ratio of 2 niobium to 5 Ethoquad was found.

A quick survey of other quaternary ammonium compounds showed that neither tetramethylammonium chloride nor benzyltrimethylammonium chloride enhanced the niobium-pyrogallol colour. Tribenzylamine and lauryltrimethylammonium chloride produced precipitates. The lauryl derivative extracted to give a spectrum

(Fig. 2) which had an absorbance at 410 mμ somewhat less than that for the aqueous Ethoquad system, and it was linear with niobium concentration. Furthermore, a large excess of the lauryl compound is necessary to attain a maximum absorbance. Extrapolation led to a combining ratio of 1 niobium to 5 lauryltrimethylammonium ions.

Extractability of the lauryl derivative prompted two further tests. In one, the failure of the niobium-pyrogallol complex to extract with ethyl acetate in the absence of the quaternary ammonium ion was demonstrated over a wide range of pH. This agrees with a very recent report[17] which tested a few simple alkyl derivatives. In the second, the Ethoquad complex was shown to extract to give a somewhat lower absorbance than the lauryl extract, but linear over a much larger range.

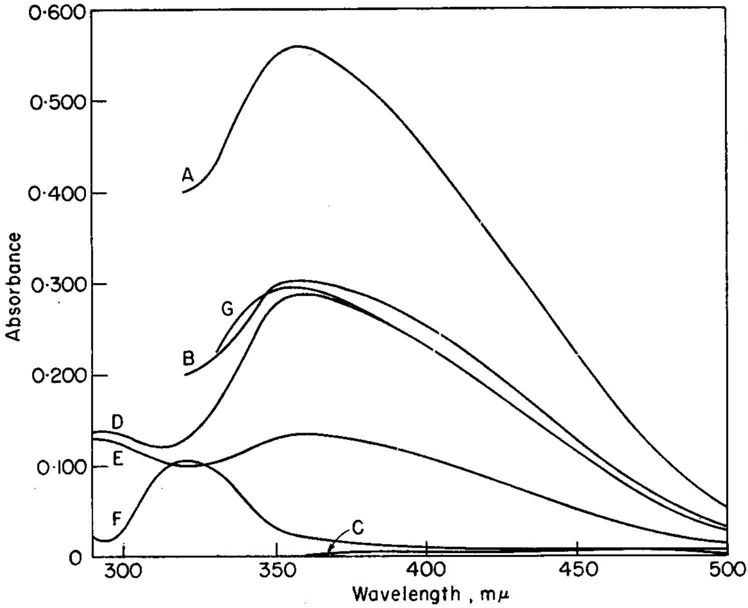

FIG. 1.—Niobium spectra showing the effects of Ethoquad and the chosen salt mixture:
Series 1 [0·8%(6·4 × $10^{-2}M$) pyrogallol]:
A—4·0 × $10^{-5}M$ Nb, 2·0 × $10^{-4}M$ Ethoquad,
B—4·0 × $10^{-5}M$ Nb,
C—2·0 × $10^{-4}M$ Ethoquad.
Series 2 [0·8% pyrogallol, 0·48%$(NH_4)_2C_2O_4 \cdot H_2O$, 2·4% Na_2SO_3, 2·5% $Na_2SO_4 \cdot 10\,H_2O$, 2·5% $(NH_4)_2HC_6H_5O_7$]:
D—2·0 × $10^{-5}M$ Nb, 4·0 × $10^{-4}M$ Ethoquad,
E—2·0 × $10^{-5}M$ Nb,
F—4·0 × $10^{-4}M$ Ethoquad,
G—same as D but 5 ml of 1*M* NaOH per 50 ml of solution present (final pH 7·5 – 7·6).

Comparative absorbance values for several modified procedures are given in Table I.

A brief study of the effect of pH on absorbance showed that an aqueous sample containing niobium-pyrogallol and Ethoquad changed less than one without Ethoquad. Within the pH range 6·4 to 8·4, the absorbance for the former went from 0·287 through a maximum of 0·333, whereas the corresponding values for the Hunt and Wells method were 0·133 and 0·211.

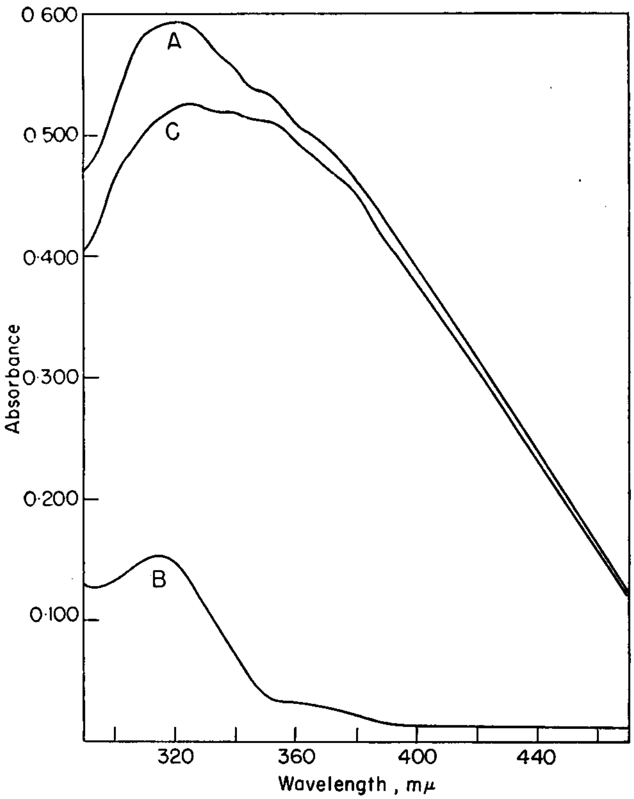

Fig. 2.—Spectra for ethyl acetate extracts of the system niobium – 0·8% pyrogallol-lauryltrimethylammonium chloride (LTMAC) and a blank:
A—4·0 × $10^{-5}M$ Nb, 2·0 × $10^{-4}M$ LTMAC,
B—4·0 × $10^{-4}M$ LTMAC,
C—differential curve (A – B/2).

Table I.—Comparative absorbance values for 4·0 × $10^{-5}M$ niobium using the original and the modified Hunt and Wells techniques

Salt system	Tetra-alkyl ammonium ion (4·0 × $10^{-4}M$)	Absorbance	
		Direct aqueous solution	Extract
Original	None	0·248	—
Original	Ethoquad	0·404	—
Original	Ethoquad	—	0·349[a]
Original	LTMAC[b]	—	0·399[c]
Proposed	Ethoquad	0·410	—
Proposed	Ethoquad	—	0·352[a]

[a] Washed with three 5-ml portions of washing solution
[b] Lauryltrimethylammonium chloride
[c] Not washed

The composition of the "salt mixture" added to the samples is not critical; it was decided upon in the following way. Because 4% ammonium oxalate solution is close to saturation and because higher concentrations would be required to hold large amounts of tantalum in solution, citrate was added as a supplement. Sulphate was added not only to stimulate the composition from a sample from an ore that had been fused with pyrosulphate but also to improve the extraction by salting out. Sodium salts were preferred to potassium salts which would precipitate potassium fluotantalate.

TABLE II.—INTERFERENCES, IN TERMS OF NIOBIUM, FROM 1 MILLIMOLE OR 1 mg OF CERTAIN METAL IONS

		I	II	III
			Ethoquad added	
Ion	Concn. units	Hunt and Wells technique[12]	Aqueous	Extract
Ta^V	mmoles	0·043	0·027	0·031
	mg	0·022	0·013	0·015
Mo^{VI}	mmoles	0·48	0·46	0·000
	mg	0·44	0·42	0·000
W^{VI}	mmoles	0·085	0·10	0·000
	mg	0·042	0·05	0·000
V^V	mmoles	no value	0·50	0·026
	mg	no value	0·90	0·047
Cr^{VI}	mmoles	not mentioned	0·009	0·000
	mg	not mentioned	0·016	0·000
Ti^{IV}	mmoles	1·09	0·96	0·77
	mg	2·11	1·85	1·49

Extraction variables

Extraction of a 25-ml aqueous sample with successive 10-, 5- and 5-ml portions of ethyl acetate removed 96% of the niobium. The last 5-ml extract contained about 3·5% of the final total.

When the extract was contacted with three 5-ml portions of wash solution, a relative loss of less than 3% was measured. As will be shown later, this loss in sensitivity for niobium is insignificant compared to the gain in selectivity afforded by the washing procedure.

Interferences

It is well known that ions of most of the elements in Groups VA and VIA interfere. Spectra for the aqueous solutions of niobium and six elements are shown in Fig. 3. The interference of each ion in terms of a unit of niobium is shown in Table II for comparison with counterparts in the original Hunt and Wells procedure.[12] In general, the figures are quite similar. However, the last column of the table together with Fig. 4 shows the striking benefits of the extraction step. Although tantalum is perhaps the most likely interference, it seems advantageous to discuss it after the other ions.

Molybdenum^{VI}. Molybdate produces an intense colour with pyrogallol in acetic acid[21] as well as in alkaline media. A combining ratio of 1 molybdate to 2 pyrogallol has been assigned to the complex between pH 6·0 and 8·0.[25] Neither the shape nor the intensity of the spectrum is affected by Ethoquad. Furthermore, it remains non-extractable. Molybdate at 100 times the concentration of niobium does not give a measurable interference. However, it was found that the absorbance at 355 mμ in the aqueous phase varies linearly with the concentration in the tested range from 2·0 × 10^{-5} to 2·0 × $10^{-4}M$, contrary to an earlier report,[20] even though pH 7·5 may not be the most favourable.[1] Up to 4·0 × $10^{-2}M$, neither phosphate nor fluoride affected the reaction.

Tungsten^{VI}. Between pH 6·0 and 8·0, a coloured species has been assigned a 1 tungstate to 2 pyrogallol ratio.[25] Ethoquad does not affect the spectrum. In addition, fluoride and phosphate up to 4·0 × $10^{-2}M$ did not affect the absorbance. At higher concentrations, they helped to retain tungsten in the aqueous phase so that fewer washings were required.

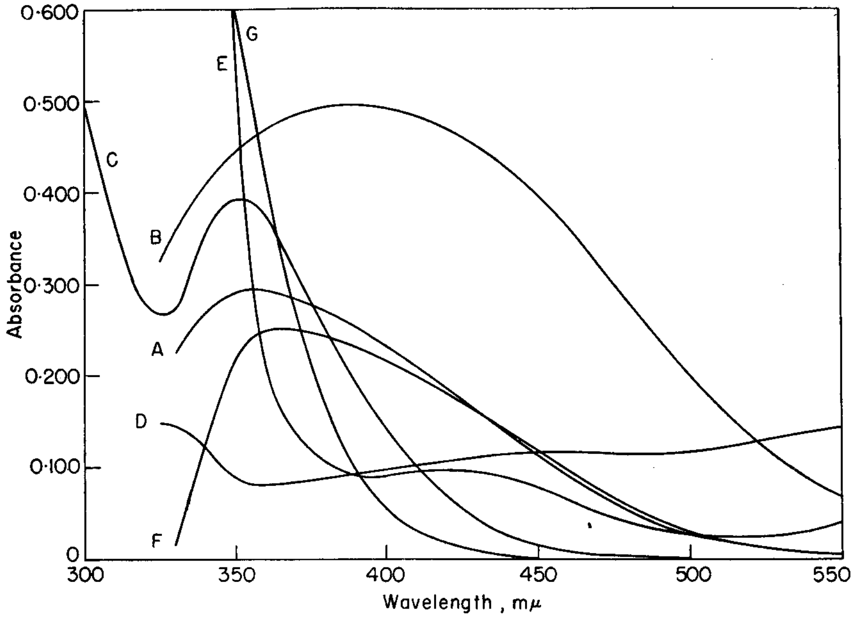

Fig. 3.—Spectra for ions in aqueous solutions prepared by the recommended procedure:
A—2·0 × $10^{-5}M$ Nb,
B—1·0 × $10^{-4}M$ Mo,
C—1·0 × $10^{-4}M$ W,
D—2·0 × $10^{-5}M$ V,
E—1·0 × $10^{-3}M$ Cr,
F—2·0 × $10^{-5}M$ Ti,
G—1·0 × $10^{-4}M$ Ta.

Vanadium^{V} Vanadate turns yellow upon acidification, but the addition of the alkaline pyrogallol reagent gives a transient purple followed rapidly by the intensely blue reduced species[18] for which the absorption peak falls beyond 800 mμ.[20] Interference is decreased by the extraction step, but it is still serious.

In an effort to reduce the interference, the reduction, extraction and washing steps were examined further. Pyrogallol, in the absence of sulphite, reduced vanadate in neutral and alkaline solutions. Ethyl acetate does not extract the reduced form, but it does extract the yellow form, the amount falling off in both acidic and alkaline media.

Vanadate cannot be extracted by ethyl acetate in the presence of Ethoquad alone, but the reduced species produced by pyrogallol is extractable on adding Ethoquad.

The presence of fluoride, phosphate, arsenate, silicate, cyanide or EDTA was not effective in avoiding reduction or in washing the reduced species (in the presence of Ethoquad) out of the extract. In fact, fluoride and phosphate did not affect the extraction significantly.

As a substitute for ethyl acetate, cyclohexane, ethyl ether, dioxane, tetrahydrofuran, dimethylformamide, di-isobutyl ketone and methyl ethyl ketone were tested. Only methyl ethyl ketone showed sufficient promise to warrant future attention.

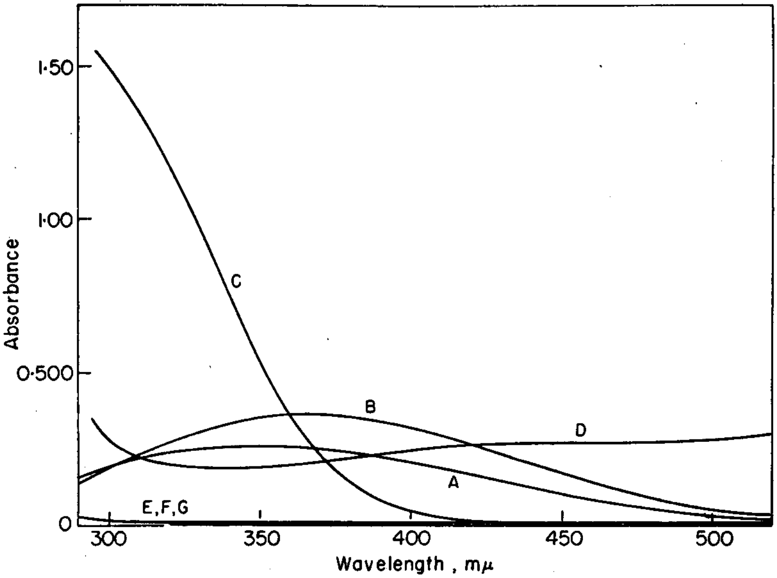

FIG. 4.—Spectra for ethyl acetate extracts obtained by the recommended procedure (extracts were dried but not washed):
A—2·0 × $10^{-5}M$ Nb,
B—4·0 × $10^{-5}M$ Ti,
C—1·0 × $10^{-4}M$ Ta,
D—1·0 × $10^{-3}M$ V,
E—2·0 × $10^{-3}M$ Mo,
F—2·0 × $10^{-3}M$ W,
G—2·0 × $10^{-3}M$ Cr.

It should be mentioned that the extracted blue colour is stable for at least 2 hr and is suitable for quantitative measurement at 410 mμ and, presumably, also above 800 mμ. After 1–2 days, a brown residue forms and the supernate is brown-yellow.

Chromium.$^{\mathrm{VI}}$ Within a few min after the addition of pyrogallol, the emerald-green reduced species is formed. Fortunately, the species is not extracted.

Titanium.$^{\mathrm{IV}}$ The yellow colour formed with pyrogallol has long been known.[9,10,24,27] Unfortunately, it is extracted in the presence of Ethoquad. Up to 4·0 × $10^{-2}M$, fluoride and phosphate had no effect. Furthermore, the extract appeared to saturate, the intensity tended to level off above 2·0 × $10^{-4}M$, so that the extract was unsuitable for the quantitative determination of titanium above that concentration.

Tantalum.$^{\mathrm{V}}$ Although tantalum is often reported not to interfere with niobium determinations, it is clear from Figs. 3 and 4 that the extent of interference depends greatly upon wavelength. The interference was unaffected by $4{\cdot}0 \times 10^{-3}M$ fluoride in excess. Using the prescribed salt mixture, at $2{\cdot}0 \times 10^{-4}M$ tantalum the aqueous solution is turbid in spite of the citrate and oxalate concentrations; the precipitate formed by $4{\cdot}0 \times 10^{-4}M$ tantalum can be dissolved by contact with $4{\cdot}0 \times 10^{-2}M$ fluoride only if allowed to stand overnight.

TABLE III.—EFFECT OF TANTALUM ON THE DETERMINATION OF NIOBIUM USING THE EXTRACTION PROCEDURE

Niobium, *M*	Tantalum, *M*	Molar ratio of Ta:Nb	Relative Errors, %	
			Direct	Corrected
$2{\cdot}0 \times 10^{-5}$	$1{\cdot}0 \times 10^{-4}$	5	+12·5	+2·3
$2{\cdot}0 \times 10^{-5}$	$2{\cdot}0 \times 10^{-4}$	10	−6·9	−27·7
$2{\cdot}0 \times 10^{-5}$	$3{\cdot}0 \times 10^{-4}$	15	−38·1	−65·3
$2{\cdot}0 \times 10^{-5}$	$4{\cdot}0 \times 10^{-4}$	20	−62·5	

[a] Absorption from tantalum deducted.

Table III, which contains typical data for mixtures of niobium and tantalum, shows that the presence of tantalum leads to a negative error, particularly if the absorbance is corrected for the expected contribution from tantalum. Because the aqueous phase after extraction was clear, adsorption losses were not the cause. By measuring a sample containing only tantalum, this element was shown to extract 87% quite consistently (in the presence of both pyrogallol and Ethoquad) up to an initial aqueous concentration of $5{\cdot}0 \times 10^{-4}M$, at which point the absorbance of the extract levelled off while that of the aqueous phase continued to increase. Therefore, the low niobium results must be caused by depletion of pyrogallol by the tantalum. The trend in absorbance with added pyrogallol (Table IV) tends to confirm this explanation although coloured oxidation products obviously contributed to the positive error at the highest concentration of pyrogallol.

TABLE IV.—EFFECT OF PYROGALLOL CONCENTRATION ON THE INTERFERENCE BY $4{\cdot}0 \times 10^{-4}M$ TANTALUM IN THE DETERMINATION OF $2{\cdot}0 \times 10^{-5}M$ NIOBIUM.

Pyrogallol, *g/50 ml*	Relative error, %	
	Direct	Corrected
0·4	−62·5	
0·8	−39·1	
2·0	+30·4	
3·0	+23·7[a]	−5·2
4·0	+44·5[a]	+15·6
5·0	+155·5[b]	

[a] Measured against a blank of 0·4 g of pyrogallol per 50 ml; no visible colour from oxidation of pyrogallol but some absorbance may have been present from that source.

[b] Noticeable off-colour from pyrogallol oxidation.

The present procedure should yield satisfactory results for niobium samples when the niobium-tantalum ratio is unity or greater. Best results would be obtained by working with a dilute sample to minimise the tantalum interference. If an independent determination of tantalum were made, the accuracy of some results for smaller ratios should be improved by applying the correction for the absorbance of tantalum.

If boric acid is added to the sample before extraction, approximately 95% of the tantalum remains in the aqueous phase. This indicates that tantalum is extracted in the form of a fluoride complex, probably TaF_7^{2-}. It also suggests a promising approach for a future study of the separation of tantalum and niobium.

Fluoride and phosphate. Concentrations of species as high as $4 \cdot 0 \times 10^{-2} M$, representing anion-to-niobium ratios of up to 2000, introduced insignificant (<2%) errors into the direct and the extraction procedures.

DISCUSSION

In the presence of a long-chain quaternary ammonium ion, the niobium-pyrogallol complex reacts to give a more highly absorbing species than otherwise and, in addition, the resulting species is extractable. The nature of the species is largely unknown although brief studies of combining ratios have indicated that 2:5 and 1:5 niobium: ammonium combinations exist.

A rapid qualitative test using the ammonium form of Dowex 50 W × 8 and the oxalate form of Dowex 3 showed little exchange of the niobium and tantalum pyrogallol-Ethoquad complexes by the former, but extensive exchange by the latter. In contrast, vanadium and chromium disappeared completely on to the cation exchanger but were unaffected (except for slow reduction of vanadium on the beads) by the anion exchanger. It appears, therefore, that interference from vanadium might be virtually eliminated by prior contact with a cation exchanger.

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Zusammenfassung—Die optische Absorption einer Mischung von Niob(V) und Pyrogallol in leicht alkalischem Medium wird um etwa 60% erhöht, wenn eine langkettige quaternäre Ammonium-Verbindungen zugesetzt wird. Zusätzlich wird die Störung durch Mo(VI), W(VI) und Cr(VI) praktisch vollkommen ausgeschaltet und die von V(V) auf die Hälfte reduziert, wenn der Niobkomplex mit Äthylacetat ausgezogen wird. Tantal wird mit ausgezogen, seine Störung kann jedoch durch geeignete Wahl der Wellenlänge wesentlich vermindert werden. Die Störung durch Ti ist erheblich, jedoch etwas geringer als in der Original Methode von Hunt und Wells.

Résumé—L'absorption optique produite par le mélange niobium(5)-pyrogallol en solution faiblement alcaline est augmentée d'environ 60% par la présence d'un sel d'ammonium quaternaire à longue chaîne. De plus, les interférences du molybdène(VI), du tungstène(VI) et du chrome(VI) peuvent être pratiquement éliminées et celle du vanadium (V) réduite de moitié en extrayant le complexe du niobium par l'acétate d'éthyle. Le tantale accompagne le niobium, mais, en choisissant convenablement la longueur d'onde, on peut diminuer l'interférence due à de faibles quantités. L'interférence du titane est trés sérieuse, mais un peu moins que dans la méthode originale de Hunt et Wells.

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IMPROVED DETERMINATION OF TANTALUM BASED UPON THE PYROGALLOL PROCEDURE

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Summary—The pyrogallol method for tantalum has been improved in two ways. First, the addition of boric acid eliminates the interference from fluoride. Second, incorporation of an extraction with ethyl acetate, in the presence of a long-chain quaternary ammonium ion, eliminates the interference from vanadium^{V} and decreases that from chromium^{VI}. Titanium^{VI}, molybdenum^{VI} and tungsten^{VI} remain as interferences.

INTRODUCTION

For a study involving the enrichment of tantalum by foam fractionation, the pyrogallol method[2–9,13,15] was preferred because of its known compatibility with the foam-producing quaternary ammonium surfactant. The adopted analytical procedure closely follows that of Hunt and Wells[6] with two exceptions. First, Ethoquad, a quaternary ammonium chloride, is added to make possible the extraction of vanadium and chromium, and thereby greatly reduce interference from these ions. Second, because hydrofluoric acid is frequently used to dissolve samples, boric acid was also added to complex free fluoride ion. The usual Hunt and Wells procedure involves fusion of a sample with bisulphate, followed by dissolution of the melt in a solution of ammonium oxalate and development of a colour with pyrogallol. The tantalum procedure is closely related to the one for niobium, the chief difference being the acidic medium used for tantalum as opposed to a weakly alkaline one for niobium.

EXPERIMENTAL

Reagents

In general, the reagents were the same as those for the determination of niobium.[1] Finely powdered ammonium oxalate (Mallinckrodt) and boric acid (Merck) were used.

Pyrogallol reagent:[6] A 5-ml portion of 1:1 sulphuric acid was added to 20 g of pyrogallol followed by 70 ml of water. After dissolution of the crystals, the solution was filtered and diluted to 100 ml with water. After 5 days, the reagent was unchanged or, at the most, slightly pink.

Wash solution: A mixture of 20 ml of $0{\cdot}5M$ sodium fluoride, 80 ml of $1{\cdot}0 \times 10^{-3}M$ Ethoquad 18/25 (polyethoxy [15] stearylmethylammonium chloride from Armour and Co.), 40 ml of 9% sodium bisulphate and 20 ml of $1M$ sodium hydroxide solution was diluted to 200 ml with distilled water. The final pH was slightly above 3·0.

Procedure

Add to an appropriate aliquot of the sample solution, as prepared by the Hunt and Wells procedure,[6] 1 g of boric acid, 20 ml of aqueous $1{\cdot}0 \times 10^{-3}M$ Ethoquad and 4 ml of pyrogallol reagent. Dilute with water to 50 ml and shake until a clear solution remains before reading the optical absorbance at 400 mμ.

When vanadate and/or chromate is present, the final solution should be extracted before measuring the absorbance. Treat 25 ml of solution successively with 10-, 5- and 5-ml portions of ethyl acetate. (These extracts after being shaken with three 5-ml portions of wash solution, then filtered through anhydrous sodium sulphate, may be used to determine vanadium or chromium by measuring the

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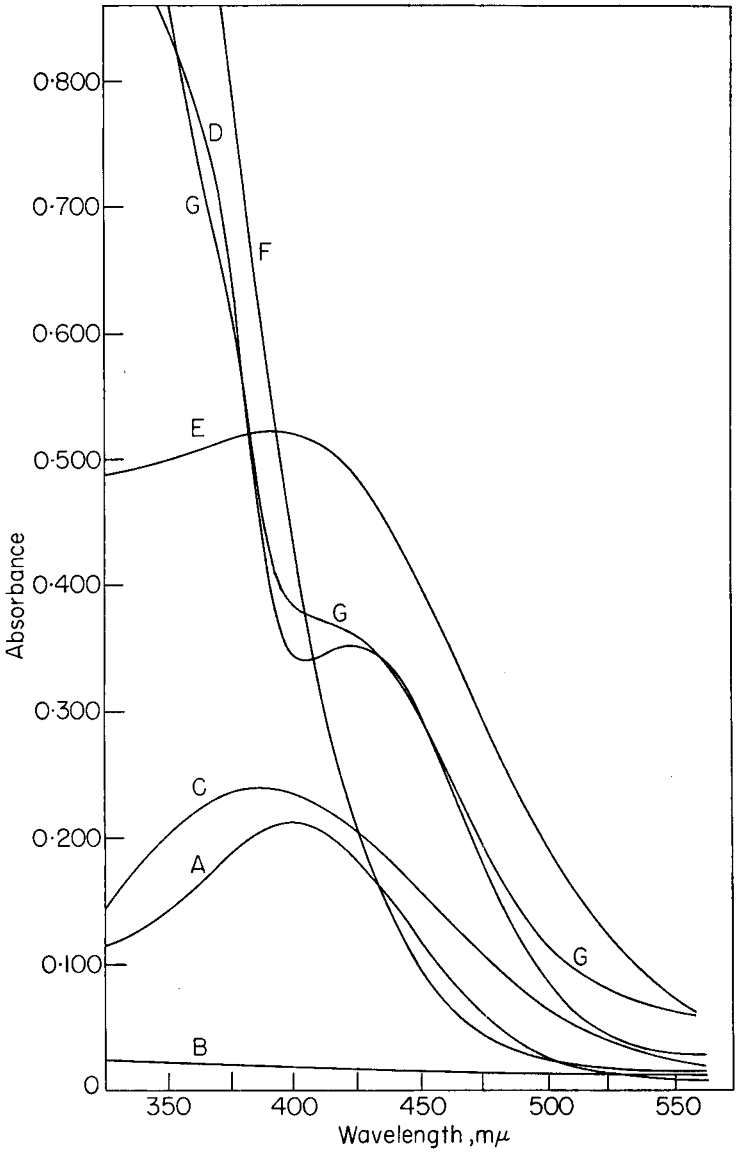

Fig. 1.—Spectra for tantalum and certain interfering ions in the aqueous solution before extraction:

A—1·0 × $10^{-4}M$ Ta,
B—2·0 × $10^{-4}M$ Nb,
C—1·0 × $10^{-4}M$ Ti,
D—1·0 × $10^{-3}M$ V,
E—5·0 × $10^{-4}M$ Mo,
F—1·0 × $10^{-3}M$ W,
G—5·0 × $10^{-4}M$ Cr,

absorbance at 420 mμ.) Tantalum remains in the original aqueous phase which is filtered through wet filter paper. The absorbance is measured on the last filtered portion, and it is linear up to $3 \times 10^{-4}M$ tantalum, the highest concentration tested, for which the absorbance was 0·645.

RESULTS

Preliminary studies

An attempt to substitute ammonium citrate for ammonium oxalate led to a large decrease in the absorbance. Even though the residual absorbance values were linear with the tantalum concentration, the sensitivity was so poor that the use of citrate was abandoned. Parenthetically, it is of interest to note that citrate enhanced the intensity of the vanadium colour without affecting its extractability into ethyl acetate.

Although earlier investigators warned of interference from excess fluoride, provisions for its elimination are seldom mentioned.[5] A few experiments confirmed that the presence of excess boric acid eliminated the fluoride interference, increased the absorbance, and produced a linear relationship with the tantalum concentration. By comparing the absorbance values for two portions of a tantalum sample, one of which has not been treated with boric acid, one should be able to measure the fluoride present.

The presence of Ethoquad was found to exert no effect upon the absorbance or the extraction behaviour of tantalum. It was retained as a reagent because it makes possible the elimination of interference from chromium and vanadium.

The pH of 3·0 to 3·2 recommended by Hunt and Wells[6] has been retained. However, it was observed that an absorbance value nearly 25% greater was obtained at pH 3·5. This emphasised the need to control carefully the final pH.

TABLE I.—INTERFERENCES, IN TERMS OF TANTALUM, FROM 1 MILLIMOLE OR 1 MG OF CERTAIN METAL IONS[a]

			$4{\cdot}0 \times 10^{-4}M$ Ethoquad added		
Ion	Concn. units	Hunt and Wells[6]	Direct	Extracted	Extracted; H_3BO_3 present
Mo^{VI}	mmoles	0·27	0·49	—	—
	mg	0·51	0·92	—	—
W^{VI}	mmoles	0·11	0·20	—	—
	mg	0·11	0·20	—	—
V^{V}	mmoles	0·26	0·16	0·035	0·00
	mg	0·92	0·57	0·125	0·00
Cr^{VI}	mmoles	not mentioned	0·36	0·093	0·093
	mg	not mentioned	1·25	0·32	0·32
Ti^{IV}	mmoles	0·99	1·09	—	—
	mg	3·74	4·12	—	—
Nb^{V}	mmoles	0·0051	0·044	0·038	—
	mg	0·0100	0·086	0·074	—

[a] Calculated for $1{\cdot}0 \times 10^{-4}M$ tantalum from the absorption of the pure interference.

Interferences

Molybdenum^{VI}. The yellow-to-orange colour is a molybdenum-pyrogallol complex for which a 2:3 ratio[12] and a 1:1 ratio at pH 3·5[10] have been reported. Unfortunately, the colour is not extracted by ethyl acetate so that its interference is serious (see Table I). Phosphate and fluoride, up to 4·0 × $10^{-2}M$ do not affect the intensity of the colour.

Tungsten^{VI}. The 1:1 tungsten-pyragallol complex at pH 3·5[10] has a greenish-yellow colour. It interferes seriously because it is not extractible. The intensity of the colour is gravely affected by fluoride; it could be increased by the presence of boric acid or completely destroyed by added fluoride. The colour could be largely destroyed by adding phosphate.

Vanadium^{V}. On adding pyrogallol, a transient violet colour appears before the solution turns yellow-orange. The vanadium-pyrogallol colour is reported[12] to have a ratio of 2:3. The intensity is decreased by boric acid, but as shown in Table I, boric acid increases the extractibility of vanadium from about 85% to 100%, thereby entirely eliminating its interference. In fact, the absorbance values for extracts obtained using the recommended procedure have been checked and found to agree, within experimental error, with the aqueous extracts before extraction. Furthermore, the relationship between absorbance and concentration was linear up to 1·0 × $10^{-3}M$ (an absorbance of 0·245).

Table II.—Effect of niobium on the determination of 1·2 × $10^{-4}M$ tantalum

Molar ratio of Nb:Ta	Absorbance	Error, %
—	0·273	—
1:10	0·271	−0·73
1:5	0·271	−0·73
1:1	0·271	−0·73
2:1	0·266	−2·56
4:1	0·253	−7·33
8:1	0·237	−13·2
16·7:1	0·228	−16·5

The intensity for vanadium in the aqueous phase is not affected by fluoride. In the presence of 4·0 × $10^{-2}M$ phosphate, partial reduction of vanadium occurs.

Chromium^{VI}. The yellow colour developed by chromium is greenish in dilute solution and brownish in concentrated solution. It is unaffected by fluoride and phosphate (up to 4·0 × $10^{-2}M$). Although the chromium colour appears to be extractible into ethyl acetate, some colour which is probably an oxidation product of pyrogallol, remains in the aqueous phase to interfere with the tantalum determination. Boric acid had no effect on the interference.

Titanium^{IV}. The yellow colour of titanium is even more sensitive than that of tantalum. A titanium-pyrogallol ratio of 1:4 has been reported to exist in weakly acidic media.[11] The colour is not extractible and hence other separation procedures such as ion exchange[5,14] must be applied.

Niobium^{V}. For unexplained reasons, the interference from niobium was found to be nearly ten times as large as that reported by Hunt and Wells.[6] Table I shows that some niobium is removed by extraction.

Table II is a representative set of data that shows the negligible interference of niobium up to a level equivalent to tantalum. At higher levels of niobium, the errors for tantalum were negative in spite of adding additional pyrogallol to counteract that lost by reaction with niobium.

DISCUSSION

This new procedure for tantalum incorporates boric acid and thereby eliminates the interference from fluoride. In fact, it has been found that the fluoride in a solution of tantalum can be determined by measuring the absorbances in the absence and in the presence of boric acid.

Another advantage of the proposed procedure is the elimination of interference from vanadium. Although the presence of citrate greatly diminishes the absorbance of tantalum, it increases that for vanadium. Hence, the use of citrate may prove to be advantageous for determining vanadium in the presence of tantalum.

Titanium and, to a lesser extent, molybdenum and chromium interfere seriously. An earlier paper[1] has pointed out the possibility of removing chromium by cation exchange. Examination of the ion-exchange behaviour of titanium and molybdenum appears to be desirable because of the possibility that they might easily be removed in this way.

The interference data in Table I were calculated on the basis of absorbance measurements for the interfering element in the absence of tantalum. Although tests of binary mixtures yielded results which generally agreed with Table I, it is important to note that niobium, instead of giving a small positive interference, actually gave a negative interference because of depletion of pyrogallol (Table II).

Another possibility which would eliminate any interference from chromium and molybdenum, would be to extract the tantalum under conditions used for niobium. Back extraction of tantalum (and much of the niobium) into an acidic aqueous medium should remove all of the interferences listed in Table I except titanium. Unfortunately, time did not permit this modification to be tested.

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Zusammenfassung—Die Pyrogallolmethode für Tantal wurde in doppelter Hinsicht verbessert. Ersten wird die Störung durch Borsäure mittels Zugabe von Fluorid ausgeschaltet. Zweitens wurde eine Extraktion mit Äthylacetat eingeschaltet, und zwar in Gegenwart einer langkettigen quaternären Ammoniumbase, wodurch die Störung durch V(V) ausgeschaltet und die durch Cr(VI) vermindert wird. Ti(IV), Mo(VI) und W(VI) stören nach wie vor.

Résumé—La méthode au pyrogallol pour le dosage du tantale a été améliorée de deux manières. D'abord, l'addition d'acide borique élimine l'interférence du fluorure. D'autre part, une extraction par l'acétate d'éthyle, en présence d'un ion ammonium quaternaire à longue chaîne, élimine l'interférence du vanadium(V) et diminue celle du chrome(VI). Il reste encore les interférence du titane(IV) du molybdène (VI) et du tungstène(VI).

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ION-EXCHANGE SEPARATIONS USING SULPHOSALICYLIC ACID*

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Summary—Ion-exchange separation of metal cations is carried out by elution from a 4- to 8-cm cation-exchange column with sulphosalicylate at pH 6 to 7. Aluminium^{III}, iron^{III}, titanium^{IV}, uranium^{VI}, vanadium^{IV} and zirconium^{IV} are quantitatively eluted, and thorium^{IV} and copper^{II} are partly eluted. Other bivalent metal ions and rare earths are quantitatively retained by the column.

A FEW investigators have used sulphosalicylic acid as a complexing agent for ion-exchange separation of metal cations. Schubert *et al.*[1] separated beryllium^{II} from copper^{II} and from uranium^{VI} using a cation-exchange column. Beryllium^{II} is eluted with sulphosalicylate at pH 3·5. Copper^{II} remains on the column and is stripped off with 3*M* sulphuric acid. In the beryllium–uranium separation, beryllium^{II} is eluted with sulphosalicylic acid adjusted to pH 4·6 to 4·7. Alimarin and Tsintsevich[2] separated gallium^{III} from zinc^{II} by elution of gallium from a cation-exchange column with pH 10 sulphosalicylate. Oliver and Fritz[3] separated several binary mixtures with fair success using either cation- or anion-exchange columns with sulphosalicylate eluent at pH 8 to 10.

A number of useful and quantitative ion-exchange separations not previously reported can be accomplished. Our separations are carried out on a very short (4- to 8-cm) cation-exchange column by elution with sulphosalicylate at pH 6 to 7. Following separation, the metal ions are determined by titration with EDTA or by other standard analytical methods.

EXPERIMENTAL

Reagents

Ion exchange resin: "Analyzed reagent" Dowex 50W X8, 100–200 mesh, sodium-form resin was used. The resin was regenerated by elution of a large batch with 3*M* hydrochloric acid, followed by an aqueous rinse and elution with 10% diammonium hydrogen citrate adjusted to pH 3·0 to 3·5 with hydrochloric acid. After another aqueous rinse, the resin was converted to the sodium form by elution with 10% sodium chloride. The resin was washed with water until a negative chloride test was obtained.

Ion-exchange paper: Reeve Angel type SA-2 ion-exchange loaded paper was used. This contains about 55% Amberlite IR-120 resin in the sodium form.

EDTA [*disodium dihydrogen(ethylenedinitrilo)tetra-acetate dihydrate*]: A 0·05*M* solution was prepared from Eastman white label material and standardised by titration of a zinc solution prepared from very pure zinc metal.

Sulphosalicylic acid: A 0·15*M* aqueous solution was used.

Acetic buffer: The solution used was 0·05*M* in sodium acetate and 0·0026*M* in sulphosalicylate. Before use, the pH was adjusted to the desired value with solium hydroxide or perchloric acid. A 0·10*M* acetate buffer was similarly prepared, but contained twice the amount of sodium acetate.

All other solutions were prepared from Reagent Grade chemicals.

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Ion-exchange paper chromatography

Strips of ion-exchange paper, 3·5 × 30·5 cm, were placed in the troughs of a chromatography cabinet. A buffer solution, 0·2*M* in ammonium acetate and 0·008*M* in sulphosalicylate, of appropriate pH, was placed in the troughs and allowed to percolate down the ion-exchange paper overnight. The papers were rinsed with water. Metal sulphosalicylate solutions were prepared by mixing 2 ml of 0·05*M* metal ion solution, 6 ml of 0·2*M* buffer and 3 ml of 0·15*M* sulphosalicylic acid. The pH was adjusted with dilute ammonia or perchloric acid. Using a 200-microlitre pipette, the samples were applied to the paper 23 cm from the bottom of the paper. The papers were eluted with 0·2*M* buffer. A dry paper was also placed in the trough to ascertain the distance travelled by the eluent. The papers were air dried, and the location of the metal ions was determined by appropriate qualitative tests.

Ion-exchange column separations

Add a slurry of Dowex 50W X8, 100–200 mesh, sodium-form resin to a 2·2 × 8-cm ion-exchange column until a resin bed approximately 4 cm high is obtained. Buffer the resin by adding 75 to 140 ml of 0·05*M* acetate buffer at a rate of 8 to 13 ml per min. The pH of the last effluent should be within 0·05 pH unit of the desired value.

To a sample mixture containing 0·05 to 0·5 mmole of each metal ion, add an amount of 0·15*M* sulphosalicylic acid equivalent to three times the molar concentration of total metal ion. Add 30 ml of acetate buffer and adjust the pH to the required value with sodium hydroxide or perchloric acid. (If titanium^{IV} is present, adjust the pH with dilute ammonia). Add the sample thus prepared to the column at a flow rate of 8 to 13 ml per min. Rinse the sample through the column with three 30-ml rinses of acetate buffer solution.

After the sulphosalicylate elution, strip the element(s) remaining on the column with strong acid. Most elements are eluted with 150 ml of 3*M* hydrochloric acid; rare earths and yttrium require 350 to 450 ml of 4*M* hydrochloric acid. Elute lead^{II} with 150 ml of 4*M* nitric acid.

Determination of metal ions

Effluents containing Al, Th, Ti, U and V must be treated with nitric and perchloric acids to destroy the sulphosalicylic acid before analysis. Evaporate the effluent to about 30 ml. Add 10 ml of concentrated nitric acid and evaporate to about 15 ml. Add 10 ml more of nitric acid and 10 ml of 70–72% perchloric acid, and evaporate to fumes of perchloric acid. Add an additional 10 ml of perchloric acid and evaporate nearly to dryness. (If Ti is present add 2 ml of concentrated sulphuric acid). Evaporate effluents containing metal ions eluted with hydrochloric or nitric acid nearly to dryness to remove excess acid before titration.

TABLE 1.—R$_f$ VALUES FOR METAL IONS ON CATION-EXCHANGE PAPER USING SULPHOSALICYLATE ELUENT

Metal ion	pH	Range of R$_f$ values	Average R$_f$
Fe^{III}	5·0	0–0·41	0·20
	6·0	0·13–0·45	0·29
U^{VI}	5·0	0–0·28	0·14
	6·0	0–0·31	0·16
Ti^{IV}	5·0		>0
	6·0		>0
Zr^{IV}	5·0		>0
	6·0		>0
Co^{II}	6·0	0	0
La^{III}	7·0	0	0
Th^{IV}	6·0	0–0·44	0·22
Y^{III}	6·0	0	0
	7·0	0	0
Cu^{II}	5·0	0·03–0·09	0·06
	6·0	0·07–0·25	0·16
Hg^{II}	6·0	0	0
	7·0	0	0
Zn^{II}	7·0	0	0
Ni^{II}	6·0	0	0
	7·0	0	0

The methods of determination used are summarised below.

EDTA: Standardise by titrating standard zinc^{II} solution using naphthyl azoxine[4] and Eriochrome Black T[5] as indicators.

Lanthanum^{III}, *yttrium*^{III}, *ytterbium*^{III}: EDTA titration using arsenazo indicator.[6]

Copper^{II}, *cadmium*^{II}, *zinc*^{II}, *cobalt*^{II}, *lead*^{II}, *nickel*^{II}: EDTA titration using naphthyl azoxine indicator.[7]

Aluminium^{III}: Addition of excess EDTA and back-titration with zinc^{II} in 50% ethyl alcohol using dithizone indicator.[8]

Thorium^{IV}: EDTA titration using Xylenol Orange indicator.[5]

Titanium^{IV}: Addition of hydrogen peroxide and excess EDTA, and back-titration with copper^{II} using naphthyl azoxine indicator.[9]

Mercury^{II}: Titration at pH 6 with 1-mercapto-2,3-diol solution using thio-Michler's ketone indicator.

Manganese^{II}: EDTA titration in the presence of ascorbic acid and potassium cyanide, Eriochrome Black T indicator.[10]

Magnesium^{II}: EDTA titration in the presence of ascorbic acid, triethanolamine and potassium cyanide, Eriochrome Black T indicator.[10]

Uranium^{VI}: Determination by the oxidation-reduction method of Sill and Peterson.[11]

Iron^{III}: Photometric titration with EDTA at 500 mμ.[12]

Zirconium^{IV}: Gravimetric determination using mandelic acid as precipitating reagent.[13]

Vanadium^{IV}: EDTA titration.[9]

RESULTS

Ion-exchange paper chromatography was used to explore the scope of sulphosalicylate elutions and to predict suitable conditions for ion-exchange column separations. The R_f values given in Table I indicated that the elution of iron^{III}, titanium^{IV}, uranium^{VI} and zirconium^{IV} is feasible at pH 5 to 7. R_f values for bivalent metal ions except copper^{II} were zero, indicating that these are not eluted.

Elution of several individual metal ions from an ion-exchange column showed that iron^{III}, aluminium^{III}, titanium^{IV} and vanadium^{IV} are quantitatively eluted at pH 6·0. Thorium^{IV} and copper^{II} are incompletely eluted. Cobalt^{II} and other bivalent metal ions are quantitatively retained by the ion-exchange column.

When quantitative separation of mixtures was attempted it was found that iron^{III}, aluminium^{III}, titanium^{IV}, uranium^{VI}, vanadium^{IV} and zirconium^{IV} are quantitatively eluted and that cobalt^{II}, cadmium^{II}, lanthanum^{III}, lead^{II}, magnesium^{II}, nickel^{II}, ytterbium^{III}, yttrium^{III} and zinc^{II} are quantitatively retained on the column. Results for typical quantitative separations are given in Table II. Although most separations were carried out on approximately equimolar binary mixtures, several successful separations were performed where the mole-ratio of eluted to retained ion was either 10:1 or 1:10.

The separation of uranium and lead failed because of the formation of a precipitate. An attempted separation of aluminium and manganese originally resulted in the elution of part of the manganese^{II} with the aluminium^{III}. However, the addition of ascorbic acid prevented any oxidation of manganese^{II} to a manganese^{III} complex, and permitted a quantitative separation of aluminium and manganese. Thorium is incompletely eluted, apparently because of the unusually high affinity of the cation-exchange resin for thorium^{IV}. The separation of aluminium^{III} and yttrium^{III} at a 1:10 mole ratio is successful only if the amount of buffer is twice the usual quantity.

Although individual results are reported in Table II, most separations were actually done in duplicate or triplicate. The average recovery for all separations was 100·5% with an average deviation of ±0·4%. The bias toward high results probably represents a pick-up of impurities from the reagents used in separation.

TABLE II.—ION-EXCHANGE COLUMN SEPARATIONS

Metal ion pairs	pH	Taken, *mg*	Found, *mg*	Difference, *mg*
Al$^{\mathrm{III}}$	6·0	6·59	6·60	+0·01
Zn$^{\mathrm{II}}$	6·0	16·44	16·44	0·00
Al$^{\mathrm{III}}$	6·1	13·22	13·23	+0·01
Zn$^{\mathrm{II}}$	6·1	3·20	3·26	+0·06
Al$^{\mathrm{III}}$	6·1	6·59	6·63	+0·04
Mn$^{\mathrm{II}}$	6·1	14·27	14·51	+0·24
Al$^{\mathrm{III}}$	6·0	6·58	6·59	+0·01
Mg$^{\mathrm{II}}$	6·0	5·44	5·47	+0·03
Al$^{\mathrm{III}}$	6·0	1·38	1·38	0·00
Mg$^{\mathrm{II}}$	6·0	10·84	10·86	+0·02
Al$^{\mathrm{III}}$	6·0	1·38	1·39	+0·01
Ni$^{\mathrm{II}}$	6·0	29·08	29·11	+0·03
Al$^{\mathrm{III}}$	6·0	6·59	6·62	+0·03
Pb$^{\mathrm{II}}$	6·0	49·43	48·10	−1·33
Al$^{\mathrm{III}}$	6·1	6·59	6·65	+0·06
La$^{\mathrm{II}}$	6·1	28·47	28·47	0·00
Al$^{\mathrm{III}}$	6·0	13·20	13·18	−0·02
Y$^{\mathrm{II}}$	6·0	5·05	5·05	0·00
Al$^{\mathrm{III}}$	6·2	1·38	1·37	−0·01
Y$^{\mathrm{II}}$	6·2	51·24	51·19	−0·05
Fe$^{\mathrm{III}}$	6·1	14·47	14·68	+0·21
Co$^{\mathrm{II}}$	6·1	14·70	14·67	−0·03
Fe$^{\mathrm{III}}$	6·1	14·45	14·48	+0·03
Ni$^{\mathrm{II}}$	6·1	14·44	14·35	−0·09
Fe$^{\mathrm{III}}$	6·1	14·45	14·45	0·00
Zn$^{\mathrm{II}}$	6·1	16·44	16·50	+0·06
Fe$^{\mathrm{III}}$	6·1	14·45	14·48	+0·03
Mg$^{\mathrm{II}}$	6·1	5·44	5·47	+0·03
Fe$^{\mathrm{III}}$	6·1	14·51	14·54	+0·03
Cd$^{\mathrm{II}}$	6·1	27·76	27·93	+0·17
Fe$^{\mathrm{III}}$	6·2	14·48	14·51	+0·03
La$^{\mathrm{III}}$	6·2	28·47	28·47	0·00
Fe$^{\mathrm{III}}$	6·2	14·48	14·54	+0·06
Pb$^{\mathrm{II}}$	6·2	49·43	49·53	+0·10
Fe$^{\mathrm{III}}$	6·3	14·54	14·54	0·00
Y$^{\mathrm{III}}$	6·3	25·47	25·47	0·00
Fe$^{\mathrm{III}}$	6·3	14·59	14·54	−0·05
Yb$^{\mathrm{II}}$	6·3	46·15	46·15	0·00
Ti$^{\mathrm{IV}}$	6·0	11·11	11·28	+0·17
Co$^{\mathrm{II}}$	6·0	14·70	14·73	+0·03
Ti$^{\mathrm{IV}}$	6·0	11·11	11·25	+0·14
Ni$^{\mathrm{II}}$	6·0	14·46	14·46	0·00
Ti$^{\mathrm{IV}}$	6·0	11·11	11·20	+0·09
Mg$^{\mathrm{II}}$	6·0	5·42	5·48	+0·06
U$^{\mathrm{VI}}$	6·2	60·18	60·05	−0·13
Cu$^{\mathrm{II}}$	6·2	16·26	16·38	+0·12
U$^{\mathrm{VI}}$	6·1	60·12	59·79	−0·33
Ni$^{\mathrm{II}}$	6·1	14·46	14·52	+0·06
U$^{\mathrm{VI}}$	6·7	60·52	60·59	+0·07
Cd$^{\mathrm{II}}$	6·7	27·82	27·98	+0·16
U$^{\mathrm{VI}}$	6·1	60·52	60·37	−0·15
La$^{\mathrm{III}}$	6·1	28·47	—	—
U$^{\mathrm{VI}}$	6·7	60·89	60·74	−0·15
Mg$^{\mathrm{II}}$	6·7	5·42	5·42	0·00
U$^{\mathrm{VI}}$	6·9	121·5	121·6	+0·1
Co$^{\mathrm{II}}$	6·9	29·46	29·46	0·00

TABLE II.—(*continued.*)

Metal ion pairs	pH	Taken, *mg*	Found, *mg*	Difference, *mg*
V^{IV}	6·1	20·20	20·22	+0·02
Co^{II}	6·1	29·49	29·49	0·00
V^{IV}	6·1	10·10	10·20	+0·10
Mg^{II}	6·1	5·42	5·33	+0·11
V^{IV}	6·0	2·42	2·48	+0·06
Zn^{II}	6·0	32·77	32·87	+0·10
Zr^{IV}	6·0	27·25	—	—
Co^{II}	6·0	14·78	14·78	0·00
Zr^{IV}	6·1	27·25	27·10	−0·15
Zn^{II}	6·1	16·40	16·43	+0·03

Zusammenfassung—Ionenaustauschertrennung von Metallionen wird erzielt, indem von 4–8 cm Säulen mit Sulfosalizylsäure bei pH 6–7 eluiert wird. Al, Fe(III), Ti(IV), U(VI), V(IV) and Zr werden quantitativ eluiert; Th und Cu(II) nur teilweise. Zweiwertige Metallionen und seltene Erden verbleiben quantitativ in der Säule.

Résumé—La séparation par échange d'ions de cations métalliques est réalisée par élution sur une colonne de 4 à 8 cm avec le sulfosalicylate à pH 6 à 7. L'aluminium(III), le fer(III), le titane(III) élués quantitativement; le thorium(IV) et le cuivre(II) ne sont élues qu'en partie. Les autres ions métalliques divalents et les terres rares sont retenus quantitativement par la colonne.

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NOTICES

(*Material for this section should be sent directly to the Associate Editor*)

CANADA

Monday–Wednesday 17–19 *September* 1962: **Ninth Ottawa Symposium on Applied Spectroscopy:** *Canadian Association for Applied Spectroscopy.* Ottawa.

Papers are invited for presentation in all fields of instrumental analysis by means of spectroscopy. This embraces emission, X-ray fluorescence and diffraction, flame emission and absorption, ultraviolet, visible and infrared absorption, nuclear magnetic resonance and mass spectroscopy.

Titles and brief abstracts of papers should be submitted before 5 June to Mr. BEN FARRAR, Programme Chairman, Ninth Ottawa Symposium on Applied Spectroscopy, J. T. Donald & Co. Ltd., 1181 Guy Street, Montreal 25, Quebec, Canada.

CZECHOSLOVAKIA

The *Association for Spectral Analysis* will be holding a meeting on **Statistical Methods in the Evaluation of Spectral Analysis Results** in mid-May in Prague.

Tuesday–Friday 3–6 *July* 1962: **Annual Meeting:** *Czechoslovak Chemical Society.* Brno.

There will be two sections dealing with analytical chemistry: *Gas Chromatography, Analysis of the Atmosphere* and *Modern Analytical Methods.*

FRANCE

Mercredi 25 *Avril–Vendredi* 4 *Mai* 1962: **6^e Salon International de la Chimie et Conférence Internationale des Arts Chimiques.**

Cette Conférence aura lieu à la Maison de la Chimie, 28, rue Saint-Dominique, Paris 7^e. Elle comprendra 19 journées scientifiques groupées sous le titre de «Journees Techniques de Paris». D'autre part, un certain nombre de manifestations se tiendront dans le cadre de la Conférence.

Vendredi 27 *Avril: Journée de Chemie Analytique Organique Examen des méthodes chimiques de l'analyse fonctionnelle*, par M. MESNARD, Professeur à la Faculté mixte de Médecine et de Pharmacie de Bordeaux.

La polarovoltrie: théories et applications à l'analyse organique, par M. P. DUBOIS, Professeur à la Faculté des Sciences de Paris.

Nouveau dispositif pour la détection et le dosage de traces de substances à l'état gazeux, par M. A. LESTIENNE, Ingénieur I.N.A. des Laboratoires de recherches Kodak-Pathé.

Les méthodes physiques ou les méthodes chimiques, par M. S. VEIBEL, Dr Phil., Professeur àl a «Polytecknisk Daereanstalt».

Mercredi 2 *Mai-Journée de l'analyse: La résonance magnétique nucléaire Allocution* par M. C. DUVAL, Directeur du Laboratoire Recherches microanalytiques de l'Ecole Nationale Supérieure de Chimie de Paris.

La résonance magnétique nucléaire. Generalites. Exposé des méthodes, par M. P. GRIVET, Professeur au Laboratoire l'Electrotechnique et de Radioélectricité de l'Université de Paris.

Applications analytiques de la résonance magnétique nucléaire du proton en chimie organique, par M. G. MAVEL, Ancien élève de l'Ecole Polytechnique, Docteur ès Sciences.

La résonance magnétique aux très basses fréquences applications à la chimie physique et à la chimie structurale, par M. G. J. BÉNÉ, Professeur à l'Université de Genève.

Aspects théoriques de la résonance magnétique nucléaire. Applications en chimie physique et en chimie analytique, par M. M. SOUTIF, Professeur de physique générale à la Faculté des Sciences de Grenoble.

Applications de la résonance magnétique nucléaire à la chimie minérale, par Melle C. ROCCHICCIOLI, Docteur ès Sciences Physiques, attachée de Recherche au Centre National de Recherche Scientifique.

Renseignements—Inscriptions à l'adresse ci-dessus.

GERMANY

Wednesday–Saturday 13–16 *June* 1962: **Fourth International Symposium on Gas Chromatography —Forty-first Meeting of European Federation of Chemical Engineering:** *Analytical Chemistry Division,* *Gesellschaft Deutscher Chemiker* and *Gas Chromatography Discussion Group, Hydrocarbon Research Group of Institute of Petroleum.* Hamburg (see also *Talanta*, 1961, **8**, 560).

The scientific programme is as follows (title of each paper is printed in the language in which it will be presented):

Wednesday Morning, 13 *June—Opening Addresses, Opening Lectures*

Professor Dr. R. Kuhn (Heidelberg, Deutschland)
Dr. A. J. P. Martin (Elstree, Herts., England)
Professor Dr. A. V. Kiselev (Moskau, UdSSR)

Wednesday Afternoon, 13 *June—Theory*

M. A. Khan (Shell Research Ltd., Chester, England)	*Non-Equilibrium Theory of Open-Tube (Capillary) Chromatographic Columns and the Effect of Interfacial Resistance on Column Efficiency.*
E. W. Chrapowa, A. V. Kiselev, R. S. Petrowa, K. D. Stscherbakowa und W. S. Wassiljewa (Chem. Fakultät der Universität Moskau, UdSSR)	*Die physikalisch-chemischen Charakteristiken der Adsorptionsprozesse an der Grenze der Phasen mit Hilfe der Gas-Chromatographie.*
J. F. K. Huber und A. I. Keulemans (Techn. Hochschule Eindhoven, Niederlande)	*Über die alineare ideale Chromatographie und die Möglichkeiten der linearen Gas-Festkörper-Chromatographie.*
C. G. Scott (Lobitos Oilfields Ltd., Cheshire, England)	*Linear Gas-Solid Chromatography.*

Panel Discussion—*Large-Scale Gas Chromatography*

Thursday Morning, 14 *June—Theory*

D. H. Desty, A. Goldup, G. R. Luckhurst and W. T. Swanton (British Petroleum Research Centre, Middlesex, England)	*The Effect of Carrier Gas and Column Pressure on Solute Retention.*
E. R. Adlard, M. A. Khan and B. T. Whitham (Shell Research Ltd., Chester, England)	*The Application Capillary Columns in the Study of the Thermodynamic Behaviour of Ethanol and Carbon Tetrachloride in Dinonyl Phthalate.*
G. F. Freeguard (University of Exeter, England) and R. Stock (Liverpool College of Technology, England)	*Some Static Measurements on Gas-Liquid-Chromatographic Systems involving Dinonyl Phthalate and Squalane.*
K.-P. Hupe und G. Wahl (Institut für Organ. Chemie der Techn. Hochschule Karlsruhe, Deutschland)	*Struktur und Selektivität von Trennflüssigkeiten.*
H. Rotzsche (Institut für Silikon- und Fluorkarbonchemie, Radebeul, Deutschland)	*Neue polare Trennflüssigkeiten mit abstufbaren Selektivitätskoeffizienten.*

Thursday Afternoon, 14 *June—Apparatus and Technique*

H. Kelker, H. Rohleder und O. Weber (Farbwerke Hoechst AG, Frankfurt/Main-Höchst, Deutschland)	*Rationalle Integrationsverfahren für die Gaschromatographie durch neue Gerätekombinationen.*
L. S. Ettre, M. J. E. Golay and S. D. Norem (Perkin-Elmer Corp., Connecticut, U.S.A.)	*A Nomographic Approach to Some Problems in Linearly Programmed Temperature Gas Chromatography.*
F. Baumann, J. F. Johnson and R. F. Klaver (California Research Corp., U.S.A.)	*Low Temperature Programmed Gas Chromatography*
R. Amos and R. A. Hurrell (Esso Research Ltd., Berks., England)	*The Design of High Efficiency Packed Columns for Use with Katharometer Detectors.*
G. Schay, G. Székely und G. Traply, (Technischen Universität, Budapest, Ungarn)	*Erfahrungen mit einer katalytischen Verbrennungszelle zur Bestimmung geringster Substanzmengen.*

Panel Discussion—*Quantitative Aspects of Gas-Chromatography with Emphasis on Detection and Data-Handling*

Friday Morning, 15 *June—Apparatus and Technique*

D. Henneberg und G. Schomburg (Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, Deutschland)	*Massenspektrometrische Identifizierung in der Gaschromatographie mit Kapillarsäulen.*
W. Hövermann und D. Jentszch (Perkin-Elmer & Co., Überlingen, Deutschland)	*Die kritische Betrachtung von Kapillarsäulen nach Golay.*

M. Mohnke (Institut für Physikal. Stofftrennung der Deutschen Akademie der Wissenschaften, Leipzig, Deutschland)	*Adsorptions-Kapillar-Chromatographie an stabilen Isotopen.*
H. Schulz (Carl Engler und Hans Bunte-Institut für Mineralölund Kohleforschung der Techn. Hochschule Karlsruhe, Deutschland)	*Kontinuierliche Stofftrennung in Gegenstrom unter den Bedingungen der Gas-Elutions-Chromatographie.*
R. Kaiser (Badische Anilin-u. Soda-Fabrik AG, Ludwigshafen, Deutschland)	*Betriebskontrolle durch automatische Prozeß-Gaschromatographie.*

Friday Afternoon, 15 *June—Applications*

D. Neylan and T. R. Phillips (UKAEA, Capenhurst, England)	*A Statistical Investigation of Factors Affecting Column Performance in the Chromatography of Inorganic Gases.*
J. Giladi and S. Sideman (Israel Institute of Technology, Haifa, Israel)	*Determination of Separation Factors from Apparently Unresolved Chromatographic Peaks.*
P. A. T. Swoboda (Agricultural Research Council, Cambridge, England)	*Quantitative and Qualitative Analysis of Flavour Volatiles from Edible Fats.*
G. Schomburg (Max-Plank-Institut für Kohlenforschung, Mülheim/Ruhr, Deutschland)	*Die Bedeutung gaschromatographischer Methoden für die Chemie der Boralkyle und Borhydride.*
D. W. Grant and G. A. Vaughan (Coal Tar Research Association, Gomersal, England)	*The Analysis of Complex Phenolic Mixtures by Capillary Column GLC after Silylation.*

Panel Discussion—*Qualitative Aspects of Gas-Chromatography with Emphasis on Identification by Retention-Data and by other Physical and Chemical Methods.*

Saturday Morning, 16 *June—Applications*

R. Berry (UKAEA, Culcheth, England)	*Analysis of Milli-Microlitre Quantities of Permanent Gas Mixtures.*
F. H. Huyten and G. W. A. Rijnders (Koninklijke/Shell Laboratorium, Amsterdam, Niederlande)	*Trace Analyses by means of Gas-Solid Chromatography.*
F. Drawert (Forschungsinstitut für Rebenzüchtung Siebeldingen über Landau/Pf., Deutschland)	*Reaktions-Gaschromatographie.*
A. I. Keulemans (Technische Hochschule, Eindhoven, Niederlande) and S. G. Perry (Esso Research Ltd., Berks., England)	*Identification of Hydrocarbons by Thermal Decomposition.*

Sunday–Friday 26–31 *August* 1962: **Thirteenth Session of the International Commission for Uniform Methods of Sugar Analysis.** Hamburg.

Further information may be obtained from the Hon. Secretary, Dr. D. Gross, Tate and Lyle Research Laboratories, Keston Kent, England.

JAPAN

Monday–Saturday 10–15 *September* 1962: **International Symposium on Molecular Structure and Spectroscopy:** *I.U.P.A.C.* and *Science Council of Japan.* Tokyo.

The Symposium will consist of a plenary session with specially invited speakers and several section meetings with lectures by invited speakers plus short communications by interested participants.

The subjects to be covered include infrared, Raman, ultraviolet and micro- and radio-wave spectroscopy. Main topics will be theory, rotation and rotation-vibration spectra for determination of molecular structures, assignment of bonds in vibration spectra, electronic spectra, spectra of unstable molecules and radicals, internal rotation, spectra of complex organic compounds, inorganic compounds, spectra and molecular interaction, techniques and applications.

Further information may be obtained from the Secretary, Organising Committee, International Symposium on Molecular Structure and Spectroscopy, Science Council of Japan, Ueno Park, Tokyo, Japan.

SWITZERLAND

Monday–Saturday 15–20 *October* 1962: **Second International Exhibition and Congress of Laboratory, Measurement and Automation Techniques in Chemistry.** Swiss Industries Fair, Basle.

In connection with the Exhibition the *Association of Swiss Chemists* and the *Swiss Association of Automatic Control* are once again organising international lecture meetings.

The sessions sponsored by the *Association of Swiss Chemists* will cover a wide variety of subjects, including various laboratory separation methods (special methods of chromatography, zone melting, crystallisation processes and flotation), determination of particle size and molecular and crystal structures, isotopic methods, electron spin resonance, rotatory dispersion, thermal analysis and X-ray fluorescence.

The sessions sponsored by the *Swiss Association of Automatic Control* will include electronic, automatic and digital methods in measuring, counting, balancing, dosing and checking chemical processes. Higher operations in automatic control (optimising, adapting and self-learning systems) will also be covered.

Further information may be obtained from M. TROTTMANN, Swiss Industries Fair, P.O. Box 21, Basle, Switzerland.

UNGARN

Der Fachausschuss für Emissionsspektralanalyse der Materialprüfungsabteilung des Wissenschaftlichen Vereins für Maschinenbau und seine Gruppe in Miskolc geben sich die Ehre, Sie davon zu unterrichten, dass die

V. Ungarische Tagung fur Emissionsspektralanalyse

mit Kooperation der Gruppe des Wissenschaftlichen Vereins für Bergbau und Hüttenwesen in Diosgyör sowie mit Teilnahme der Technischen Universtät für Schwerindustrie in Miskolc

in der Zeit vom 9. bis 10 August in Miskolc

stattfindet.

Thematik der Tagung: *Emissionspektralanalyse in Hüttenwesen.*

Zeil der Tagung ist, ein umfassendes Bild über die Rolle der Emissionsspektralanalyse im Metallhüttenwesen—in erster Linie im Eisenhüttenwesen—, über ihre Anwendungsmöglichkeiten und Probleme sowie über die zukünftlichen Aufgaben derselben zu geben. Nach der Abhaltung der Tagung können einige Werke des Industriegebietes sowie die Naturschönheiten und Sehenswürdigkeiten von Borsod und Umgebung besichtigt werden.

Die Hauptvorträge werden von heimischen Fachleuten in ungarischer Sprache gehalten. Die Texte der Hauptvorträge werden unseren werten ausländischen Gästen in deutscher Sprache zur Verfügung stehen.

Weitere Auskunft ist von Dr. K. Zimmer, G.T.E. V. Szabadság tér 17, Budapest, zu erhalten.

UNITED KINGDOM

Tuesday 1 *May* 1962: **Joint Meeting:** *Physical Methods Group and Midlands Section, Society for Analytical Chemistry* and *Birmingham and Midlands Section, Royal Institute of Chemistry.*

The following programme has been arranged:

2.15 p.m.—Visit to the Analytical Section, Caswell Research Laboratories, Plessey Co. Ltd., Towcester.

6.15 p.m.—*Spectrographic Determination of Some Impurities in Gallium Arsenide:* Mr. J. H. OLDFIELD and Mr. D. L. MACK; *Radioactivation Analysis of Semi-conductors:* Mr. D. HAZELBY; *Determination of Carbon and Silcon in Gallium Arsenide*: Mr. J. M. PAGE and Mr. D. C. NEWTON. College of Technology, St. George's Avenue, Northampton.

Wednesday 2 *May* 1962: **Symposium on the Determination of Sterols:** *Society for Analytical Chemistry.* Welcome Building, Euston Road, London, N.W.1. Afternoon and evening meeting.

The following papers will be presented:

G. S. BOYD (University of Edinburgh)	*Determination of Cholesterol for Clinical Purposes.*
E. KODICEK (Dunn Nutrition Laboratory, Cambridge)	*Determination of Vitamin D Secosterols.*
C. J. W. BROOKS (Western Infirmary, Glasgow)	*Gas Chromatographic Examination of Sterols.*
K. R. BEERTHUIS (Unilever Research Laboratorium, Vlaardingen, Holland)	*Determination of Animal in Vegetable Fats by Gas Chromatographic Analysis.*
J. GLOVER (University of Liverpool)	*Determination of Cholesterol and Its 7-Dehydro Derivatives.*
T. W. GOODWIN (University College of North Wales)	*Determination of Plant Sterols.*
E. V. TRUTER (University of Leeds)	*Determination of Sterols of Wool Wax and Related Materials.*

Tuesday 8 *May* 1962: **Neutron Activation Analysis:** Professor H. M. N. H. IRVING: *Chemical Society* and *Edinburgh University Chemical Society.* Chemistry Department, University, Kings Buildings, West Main Road, Edinburgh. 4.30 p.m.

Friday 11 *May* 1962: **Joint Meeting:** *Microchemistry Group and Midlands Section, Society for Analytical Chemistry.* Technical College, Luton.

There will be an afternoon visit to Rothamstead Experimental Station.

Tuesday–Friday 18–21 *September* 1962: **First International Congress of Food Science and Technology.** Imperial College of Science and Technology, South Kensington, London, S.W.7 (see also *Talanta*, 1961, **8**, 690).

The following parts of the lecture programme are of interest to analytical chemists:

Section C—Quality, Analysis and Composition of Foods

1. *Specialised Analytical Techniques*

H. C. MANNHEIM and S. ZIV	*A Pectin Esterase Activity Test as an Index of Sufficient Heat Treatment for Citrus Products.*
W. J. W. LLOYD and T. L. PARKINSON	*Polarographic Determination of Dissolved Oxygen in Beverages with Reference to Carbonated Drinks.*
T. L. PARKINSON and W. J. W. LLOYD	*Determination of Saccharin in Still and Carbonated Fruit Drinks and Mineral Waters.*
C. PAQUOT	*Methods of Determining the Stability of Oils and Fats.*
J. P. WOLFF	*Application of Gas Chromatography to the Control of Purity of Fatty Substances.*
R. MARCUSE	*Automatic Determination of Oxygen Consumption during Rancidification Processes.*
R. SAWYER	*Some Aspects of the Use of Microbiological Assays in the Laboratory of the Government Chemist.*
J. E. FORD, M. E. GREGORY and S. Y. THOMPSON	*Measurement of Vitamin B in Foods: Comparative Tests with Different Micro-Organisms.*
F. WOKES and F. W. NORRIS	*Use of Microbiological Assays in Measuring Changes in the B Vitamins in Foods and Raw Materials during Germination (Seeds), Production and Storage (Eggs) and Manuring (Vegetables).*
H. FINK	*Newer Experiences at Determination of Biological Quality in Experiments on Animals.*
J. R. BISHOP	*Rapid Gas Analysis by Simple Gas-Solid Chromatography.*
A. PRACHANKADEE and B. S. LUH	*Extraction, Characterisation and Gas Chromatography of Capsaicin in Capsicum.*
W. H. STAHL, W. A. VOELKER and J. H. SULLIVAN	*New Physico-Chemical Methods of Analysis of Vanilla Extract.*
B. J. RUSHBRIDGE	*Application of the Direct Reading Spectrophotometer to Food Analysis.*
J. SIVADJIAN	*Hygrophotographical Recording Method for Moisture Content of Foods and for Permeability of Food Packaging Materials to Water and Moisture.*
E. EAST	*Polarographic Determination of Sulphur Dioxide in Foodstuffs.*
J. L. BUCHAN	*Sugars in Foodstuffs—Some Newer Methods of Analysis.*
S. JACOBS	*Determination of Nitrogen in Food Diets by the Indanetrione Hydrate Method.*
C. E. ALBERTSSON	*Automatic, Continuous Determination of Diastatic Activity of Cereals.*
J. B. MONSEY and D. H. SHRIMPTON	*Use of an α-Amylase Test for Pasteurised Liquid Whole Egg.*

2. *Detection and Determination of Minor Constituents*

E. Q. LAWS	*Residues from Agricultural Pesticide Treatment.*
C. G. HUNTER	*Analysis of Agricultural Pesticides in the Mammalian Body.*
J. F. C. TYLER	*Ethylenethiourea: Its Occurrence in Fungicides and Detection in Fruit.*
L. W. MAPSON	*Methods for Detection and Estimation of* l-*Ascorbic Acid and Dehydro*-l-*ascorbic Acid in Foods.*

H. B. Hawley and G. G. Fowler	*Detection and Assay of Nisin in Foodstuffs.*
N. W. R. Daniels, P. W. Russell Eggitt and J. B. M. Coppock	*Isolation and Identification of a Trace Constituent in the Lipid of Chlorinated Cake Flour.*
4. *Objective Methods of Quality Assessment*	
P. A. T. Swoboda	*New Techniques in the Gas Chromatographic Analysis of Flavour .*
5. *Establishment and Operation of Quality Control*	
H. M. Glass	*Methods of Sampling and Testing Foods at the National and International Standards Levels.*

The following have been elected Officers and Members of Council of the **Society for Analytical Chemistry** for the forthcoming year:—

President: A. J. Amos.
Past Presidents serving on Council: R. C. Chirnside, J. H. Hammence, D. W. Kent-Jones, K. A. Williams.
Vice-Presidents: A. L. Bacharach, J. R. Edisbury, F. C. J. Poulton.
Hon. Treasurer: D. T. Lewis.
Hon. Secretary: R. E. Stuckey.
Hon. Assistant Secretaries: C. A. Johnson (Programmes), S. A. Price.
Ordinary Members of Council: H. E. Brookes, S. G. Bugess, P. F. S. Cartwright, R. A. Chalmers, B. S. Cooper, D. C. Garratt, J. F. Herringshaw, S. H. Jenkins, C. A. Parker, R. M. Pearson, A. A. Smales, D. W. Wilson.
Ex-Officio Members of Council: J. Markland (Chairman, North of England Section), A. F. Williams (Chairman, Scottish Section), F. H. Pollard (Chairman, Western Section), H. C. Smith (Chairman, Midlands Section), C. Walley (Chairman, Microchemistry Group), W. Cule Davies (Chairman, Physical Methods Group), J. S. Simpson (Chairman, Biological Methods Group).

The following have been elected Officers of the **Midlands Section, Society for Analytical Chemistry** for the forthcoming year:—

Chairman: Dr. H. C. Smith
Vice-Chairman: Mr. W. H. Stephenson
Hon. Treasurer: Mr. F. C. Poulton
Hon. Secretary: Mr. G. W. Cherry, 48, George Frederick Road, Sutton Coldfield, Warwickshire.

The following have been elected Officers of the *Microchemistry Group* of the *Society for Analytical Chemistry* for the forthcoming year:

Chairman: Mr. C. Walley
Vice-Chairman: Miss M. Corner
Hon. Treasurer: Mr. G. Ingram
Hon. Secretary: Mr. D. W. Wilson, Chemistry Department, Sir John Cass College, Jewry Street, Aldgate, London, E.C.3.

BSI News announces the following *Revised British Standard:*
B.S. 1416:1962: *Methods for the sampling and analysis of rennet casein.* This deals with the sampling of rennet casein and provides methods of determination of dirt, particle size, moisture, ash, fat, pH and iron. Determination of the colour of untreated and wet-heat treated rennet casein is provided for by reference to B.S. 1416 C. (Price 5s.).

The following Amendment Slip is also announced:
B.S. 1728: *Methods for the analysis of aluminium and aluminium alloys: Part 12: 1961: Determination of silicon (absorptiometric molybdenum blue method). Amendment No. 1: PD 4423.*

UNITED STATES OF AMERICA

The Federal President of Austria has bestowed on Dr. A. A. BENEDETTI PICHLER the **Austrian Honorary Insignia for Arts and Sciences.** The presentation was made by the Acting Consul General, Dr. JOHANNA NESTOR, at the Austrian Consulate General, New York, on 18 January, 1962. A small group of friends and students of Dr. BENEDETTI PICHLER were invited to participate in the ceremony.

Dr. BENEDETTI PICHLER was born in Austria and taught microchemistry at the Technische Hochschule in Graz, where he worked under Dr. FRIEDRICH EMICH, one of the pioneers in the field of microchemistry. He was also a student of Dr. FRITZ PREGL who was awarded the Nobel Prize in 1933 for his contributions to organic microchemical analysis. In 1930 he came to the United States and taught chemistry at New York University and Brooklyn College. Since 1940 he has been on the faculty of Queens College in Flushing, N.Y., where he is Professor of Chemistry.

The Insignia was given to Dr. BENEDETTI PICHLER for his work in the fields of macro-, micro- and submicro-chemistry, for his numerous publications, especially for his text books and contributions to treatises on analytical chemistry, and for his teaching of analytical and general chemistry both in Austria and in the United States.

Thursday 19 *April* 1962: **Thin Layer Chromatography:** Dr. E. WOLLISH: *Metropolitan Microchemical Society.*

Monday 30 *April–Thursday* 3 *May* 1962: **Thirteenth Annual Mid-American Spectroscopy Symposium:** *Society for Applied Spectroscopy, Chicago Section* in co-operation with *Cleveland, Detroit, Indianapolis and St. Louis Sections.* Conrad Hilton Hotel, Chicago (see also *Talanta*, 1961, **8,** 914).

Tuesday–Thursday 1–3 *May* 1962: **Seventeenth Purdue Industrial Waste Conference.** Purdue University, Lafayette, Ind.

Tuesday 8 *May* 1962: **Solid State Lasers:** Dr. L. M. VALLESE. *Society for Applied Spectroscopy, New York and Philadelphia Sections.* Princeton Inn, Princeton, New Jersey.

June–August 1962: **Gordon Research Conferences for 1962.** The following Conferences will be of special interest to analytical chemists:—

Conference on Analytical Chemistry. New Hampton School, New Hampton, New Hampshire:

Monday 13 *August*	
KLAUS BIEMANN	*Mass Spectra of Complex Organic Molecules.*
A. P. ALTSHULLER	*Trace Analysis in Vapours and Gases.*
Tuesday 14 *August*	
W. H. REINMOUTH	*Voltammetry with Periodically Varying Signals.*
Open discussion on *Electrochemical Methods.*	
Wednesday 15 *August*	
J. M. BOBBITT	*Thin Layer Chromatography.*
L. R. SNYDER	*Theory and Applications of Linear Elution Adsorption Chromatography.*
Thursday 16 *August*	
J. CALVIN GIDDINGS	*Principles of Gas Chromatography.*
Open session	
Friday 17 *August*	
STANLEY BRUCKENSTEIN	*Non-Aqueous Acid-Base Equilibra.*

Conference on Infrared Spectroscopy. Kimball Union Academy, Meriden, New Hampshire:

Monday 27 *August*	
E. B. WILSON	*Rotational Barriers.*
N. SHEPPARD	*Rotational Isomerism.*
J. DECIUS	*Infrared Spectra of Solid Solutions.*

Tuesday 28 *August*

H. W. THOMPSON	*Quantitative Raman Spectroscopy.*
B. STOICHEFF	*Masers as Spectroscopic Sources.*
R. A. SMITH	*Recent Developments in Infrared Detectors.*

Wednesday 29 *August*

J. LINNETT	*Potential Functions.*
D. HORNIG	*Potential Functions in Hydrogen Bonding.*
E. R. LIPPINCOTT	*Effects of High Pressure in Infrared Spectra.*

Thursday 30 *August*

J. SCHACHTSCHNEIDER	*Group Frequencies and the Transference of Force Constants.*
D. M. DENNISON	*Utility of Normal Co-ordinate Calculations.*

Speaker and subject to be announced.

Friday 31 *August*

J. POLANYI	*Infrared Chemiluminescence.*

Speaker and subject to be announced.

Further information and registration forms may be obtained from the Director of the Gordon Conferences, W. GEORGE PARKS, University of Rhode Island, Kingston, Rhode Island, U.S.A.

Sunday–Thursday 16–20 *September* 1962: **Second Annual Conference on Pharmaceutical Analysis.** King's Gateway, Land O'Lakes, Wisconsin.

The preliminary condensed scientific programme is as follows:

Monday 17 *September*

9.00 a.m.–12.30 p.m.	*Instrumentation and Physical Techniques:* Recent Developments in NMR Techniques. Applications of X-Ray and Electron Diffraction to Pharmaceutical Analysis.
8.00–10.00 p.m.	Informal discussion in Actual Usage Experience of the above two methods.

Tuesday 18 *September*

9.00 a.m.–12.30 p.m.	*Analysis of Dosage Forms—Problems related to Control and Analysis of Single Unit Doses:* The Problem of Variations among Unit Doses. Statistics of Unit Dose Control.
8.00–10.00 p.m.	Analytical Problems related to Control of Unit Doses.

Wednesday 19 *September*

9.00 a.m.–12.30 p.m.	*Body Fluid Analysis—Detection and Determination of Basic Nitrogenous Drugs in Body Fluid:* Acid-Dye Technique.
8.00–10.00 p.m.	Open discussion on conference topics.

Thursday 20 *September*

9.00 a.m.–12.30 p.m.	*Body Fluid Analysis* (continued): Informal Presentation of Some Specific Methods for Determination of Basic Nitrogenous Drugs in Body Fluid.

Further details and registration forms (deadline—15 June) may be obtained from the Conference Secretary, RICHARD S. STROMMEN, University of Wisconsin, Extension Services in Pharmacy, Madison 6, Wis., U.S.A.

Wednesday 31 *October–Saturday* 3 *November* 1962: **Ninth National Vacuum Symposium:** *American Vacuum Society.* Statler Hilton Hotel, Los Angeles, California.

The Programme Committee solicits contributed papers on all phases of vacuum technology—work related to either the theory or practice of the production, measurement or use of vacua is pertinent. The deadline date for submission of abstracts is 1 July, and the corresponding deadline for submission of final manuscripts is 15 September. Abstracts should be sent to the Chairman of the Programme Committee, Dr. G. H. BANCROFT, Consolidated Vacuum Corporation, 1775 Mt. Read Boulevard, Rochester 3, New York, U.S.A.

PAPERS RECEIVED

Mixed chemiluminescent indicators—II: The chemiluminescence of luminol and hemin: L. Erdey, W. F. Pickering and C. L. Wilson. (25 *January* 1962).

The determination of nitrate in water: G. A. F. Harrison. (26 *January* 1962).

Salting-out chromatography—VIII: Analysis of mixtures of monoalkyl esters of alkanephosphonic acids and dialkyl esters of phosphoric acid: A. Varon, F. Jakob, K. C. Park, J. Ciric and Wm. Rieman III. (27 *January* 1962).

Rifamycin—XXIV: Amperometric titrations of rifamycin B, rifamycin O, rifamycin S and rifamycin SV: Gian Gualberto Gallo, Luigi Chiesa and Piero Sensi. (29 *January* 1962).

Applications of infrared spectroscopy—VIII: The differentiation of esters and acetals from ethers in the Zeisel alkoxyl reaction: D. M. W. Anderson and J. L. Duncan. (30 *January* 1962).

Separation of certain cations from mixtures of various cations on ion-exchange papers—I: Silver and thallium: Joseph Sherma. (30 *January* 1962).

Titrimetric analysis with chloramine-T—V: Titrations in hydrochloric acid media using iodine monochloride as a reaction intermediate: E. Bishop and V. J. Jennings. (1 *February* 1962).

Titrimetric analysis with chloramine-T—VI: The chloramine-T-antimony^{III} reaction: E. Bishop and V. J. Jennings. (1 *February* 1962).

Titrimetric analysis with chloramine-T—VII: The chloramine-T-hydrazine reaction: E. Bishop and V. J. Jennings. (1 *February* 1962).

The I-Q recorder and its application to rapid coulometric analysis and micro-coulometry: Shigeki Hanamura. (5 *February* 1962).

Isotopic dilution analysis by solvent extraction—IV: Selective determination of traces of copper with dithizone: Jaromir Růžička and Jiří Starý. (6 *February* 1962).

Applications of infrared spectroscopy—IX: The behaviour of thioalkyl compounds under Zeisel reaction conditions: D. M. W. Anderson and S. S. H. Zaidi. (13 *February* 1962).

Analytical application of second order electrons: John O. Frohliger and Ronald T. Pflaum. (14 *February* 1962).

The determination of major and minor alkalies in silicates by differential flame spectrophotometry: C. O. Ingamells. (20 *February* 1962).

Analytical use of the sorption of metal complexes of 1,10-phenanthroline and related compounds on silica: F. Vydra and V. Markova. (19 *February* 1962).

Reaction of cadmium with oxine: Roger D. Whealy and B. J. Bland. (22 *February* 1962).

Analytical applications of Xylenol Orange—VI: A spectrophotometric study of the niobium-Xylenol Orange complex: K. L. Cheng and B. L. Goydish. (22 *February* 1962).

Applications of infrared spectroscopy—VII: Investigation of a reported anomalous Zeisel alkoxyl reaction: D. M. W. Anderson, M. A. Herbich and S. S. H. Zaidi. (23 *February* 1962).

Talanta, 1962, Vol. 9, p. 408. Pergamon Press Ltd. Printed in Northern Ireland

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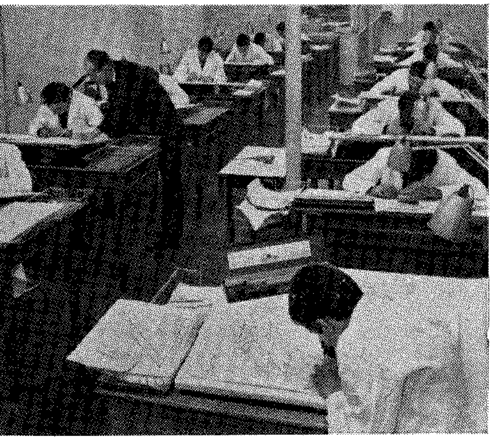

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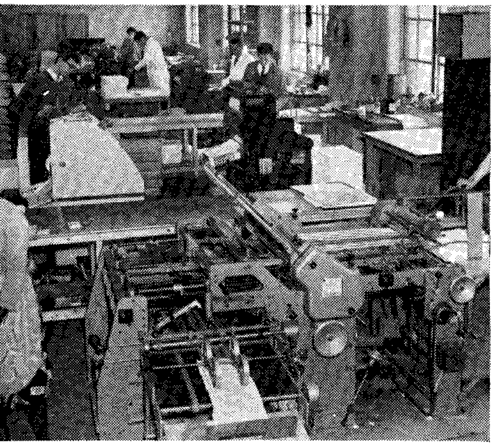

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