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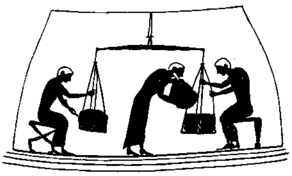

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VERFAHREN ZUR BESTIMMUNG GERINGER MENGEN, DAS JOD IN VERSCHIEDENEN OXYDATIONSZUSTÄNDEN ENTHALTENDER JODVERBINDUNGEN NEBENEINANDER

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Zusammenfassung—Ein aus Jodid, Jod, Hypojodit, Jodat und Perjodat bestehendes System ist labil und kann nur bei höheren pH-Werten und nur vorübergehend existieren. Verfasser reduzierten das Perjodat nach Zersetzung des Hypojodits mittels Phenol mit Hilfe einer überschüssigen Menge arseniger Säure und titrierten deren Überschuss zurück. Das Jodat wurde nach Reduktion des Jods und Hypojodits mittels Phenol jodometrisch bestimmt. In Gegenwart von Perjodat muss die dem Perjodat äquivalente, durch die Arsenit-Reduktion des Perjodats gebildete Menge Jodat in Abzug gebracht werden. Die gesamte Menge Hypojodit und Jod wurde aus der Differenz der jodometrischen Messungen (mit und ohne Phenol) berechnet. Nach Bestimmung der Gesamtmenge der oxydierenden Stoffe kann die Gesamtmenge Jodid in Gegenwart von p-Äthoxychrysoidin als Adsorptionsindikator mit Silbernitrat gemessen werden. In Abwesenheit von Perjodat wurde das elementare Jod neben Hypojodit unter Ausnutzung jenes Prinzips bestimmt, wonach das Thiosulfat durch Hypojodit zu Sulfat, durch Jod aber zu Tetrathionat oxydiert wird. Letzteres konnte nach dem Verfahren von Kurtenacker und Fritsch ermittelt werden. Die Ergebnisse sind zufriedenstellend.

JODVERBINDUNGEN, die das Jod in verschiedenen Oxydationszuständen enthalten, können im allgemeinen nur in einem bestimmten pH-Bereich nebeneinander existieren.

Elementares Jod, Jodid und Hypojodit können nebeneinander etwa zwischen pH = 7 und 13 bestehen, bei niedrigeren pH-Werten verschiebt sich das zwischen den Komponenten bestehende Gleichgewicht:

$$J_3^- + OH^- \rightleftharpoons JOH + 2J^- \qquad (1)$$

vollkommen in Richtung des Jods, bei höheren pH-Werten in Richtung des Hypojodits. Obige Gleichung lässt auch den Einfluss der Jodid–Konzentration erkennen. Hinsichtlich der Klärung der kinetischen Verhältnisse dieser Reaktion sind die Untersuchungen Skrabals[1] von grundlegender Wichtigkeit. Die Frage wird durch die rasche Disproportionierung des Hypojodits zu Jodat noch weiter erschwert:

$$3JO^- = JO_3^- + 2J^- \qquad (2)$$

Jodat und Jodid können über pH = 8 auch längere Zeit hindurch nebeneinander existieren, bei einem niedrigeren pH-Wert spielt sich jedoch die allgemein bekannte—auch zur Messung der Wasserstoffionen verwendbare—Reaktion

$$JO_3^- + 5J^- + 6H^+ = 3J_2 + 3H_2O \qquad (3)$$

bereits ab.

Die Reaktion zwischen Perjodat und Jodid[2] läuft unter Bildung von Jodat und Jod (bzw. in Abhängigkeit vom pH-Wert auch Hypojodit) bei pH = 8 bereits ab,

$$JO_4^- + 2J^- + H_2O = JO_3^- + J_2 + 2OH^- \qquad (4)$$

wird jedoch bei höheren pH-Werten derart langsam, dass die beiden Ionen (JO_4^- und J^-) vorübergehend auch nebeneinander bestehen können.

Beim Ansäuern wird das Perjodat vollkommen reduziert:

$$JO_4^- + 7J^- + 8H^+ = 4J_2 + 4H_2O \qquad (5)$$

Auch die obigen Reaktionsgleichungen lassen erkennen, dass bei dauernd hohem pH-Wert nur das Jodat–Jodid System existiert, alle anderen Komponenten gehen in dieses über, bei niedrigem pH-Wert hingegen führen die Prozesse zur Bildung von Jod (bzw. dem Jodid–Komplex des Jods).

Die analytische Untersuchung dieser miteinander in verwickelten Gleichgewichten stehenden Systeme ist—besonders bei niedrigen Konzentrationen—eine schwere und bisher noch ungelöste Aufgabe.

Lonnes[3] schlägt zur Bestimmung von Jod, Hypojodit und Jodat nebeneinander die kolorimetrische Ermittlung des Jods, Titration des Hypojodits und Jods mit Arsenit in der ursprünglichen (alkalischen) Lösung und nach Ansäuern Titration des aus dem Jodat ausgeschiedenen Jods mit Thiosulfat vor. Mit dieser Frage beschäftigte sich auch Péchard.[4] Sammet[5] bestimmt die Summe des Jods und Hypojodits sowie das Jodat nach ähnlichen Prinzipien, bestimmt das Jod bzw. das Hypojodit jedoch nicht getrennt. Demgegenüber ermittelt er das gesamte Jod (inbegriffen auch das Jodid) in Form von elementarem Jod in einem neuen Anteil der Lösung nach einer auf eine Reduktion drauffolgenden milden Oxydation. Der so freigemachte Gesamtjod wird nun mit Tetrachlorkohlenstoff ausgeschüttelt und gemessen. Mit der Bestimmung von Perjodat, Jodat, Jod und Jodid nebeneinander beschäftigten sich Scharrer und Schwaibold.[6]*

Wir beschäftigten uns zuerst mit der Bestimmung von relativ viel Jodid, elementarem Jod und Hypojodit nebeneinander d.h. also mit der Bestimmung des Jods mit den Oxydationszahlen -1, 0 *und* $+1$. Da zwischen diesen Formen ein Gleichgewicht besteht, musste ein Reagenz gefunden werden, das sowohl mit elementarem Jod, als auch mit Hypojodit, jedoch mit beiden auf andere Art reagiert. Diesem Zweck entspricht das Phenol nicht (obzwar es die Bestimmung von Jodat in Gegenwart von Jod bzw. Hypojodit ermöglicht[7]), da das im Überschuss angewandte Phenol das Gleichgewicht zwischen dem elementaren Jod und Hypojodit verschiebt. Kolthoff empfiehlt dieses Verfahren in der deutschen Ausgabe seines bekannten Handbuches[8] nach der Besprechung der erwähnten Methode[7] zur Analyse der Preglschen Lösung (ein Jodat, Jod und Hypojodit enthaltendes Gemisch, wahrscheinlich borathaltige alkalische Lösung des Jods) ohne nähere Bezeichnung.

Zur Lösung der Aufgabe ist das Thiosulfat geeignet, das durch Jod mit annähernd der gleichen Geschwindigkeit zu Tetrathionat und durch Hypojodit zu Sulfat oxydiert wird:[9]

$$2S_2O_3^{2-} + J_2 = S_4O_6^{2-} + 2J^- \qquad (6)$$

$$S_2O_3^{2-} + 4JO^- + H_2O = 2SO_4^{2-} + 4J^- + 2H^+ \qquad (7)$$

Hierzu möchten wir erwähnen, dass die direkte Titration mit Thiosulfat—insbesondere im 0,01 n Massstabe—nach unseren Erfahrungen nicht zum Erfolg führt, obzwar einige Autoren dieses Verfahren empfehlen.[4]

Die Ursache hierfür liegt nach den Ergebnissen unserer Untersuchungen einesteils in der Unsicherheit der Indikation (pH $\geqq$ 8) und anderenteils darin, dass das bei der

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* Die nur im Referat zur Verfügung stehende Beschreibung des Verfahrens ist uns unüberblickbar.

Jod-Thiosulfat Reaktion gebildete Tetrathionat durch Hypojodit—zumindest teilweise—gleichfalls zu Sulfat oxydiert werden kann. Die Ergebnisse sind weiter von der Geschwindigkeit der Titration abhängig. Auch die Konzentration des Hypojodits kann nach unseren Untersuchungen bei relativ niedrigen Jodid-Konzentration in einer Jodhaltigen Lösung bei pH = 8 nicht mehr vernachlässigt werden. Dies liefert die Erklärung dafür, dass das Jod bei pH = 8 im 0,01 n Massstabe mit Thiosulfat nicht mehr direkt titriert werden kann. Liegt die Jodid-Konzentration höher, so kann der Endpunkt nicht mehr oder nur ungenau beobachtet werden. Die Thiosulfatlösung muss also im Überschuss und auf einmal zugegeben werden.* Der Überschuss wird bei pH = 8 auf Stärkelösung als Indikator mit Jodlösung zurücktitriert. Der Tetrathionat-Gehalt der Lösung lässt sich—gemeinsam mit dem bei der Rücktitration des Thiosulfatüberschusses gebildeten Tetrathionat—nach der Methode von Kurtenacker und Fritsch[10] bestimmen. Das Verfahren beruht darauf, dass das Tetrathionat mit Cyanid in neutralem oder schwach alkalischem Medium nach folgender Gleichung reagiert:

$$S_4O_6^{2-} + CN^- + H_2O = S_2O_3^{2-} + SCN^- + 2H^+ + SO_4^{2-} \qquad (8)$$

Das gebildete Thiosulfat kann unter geeigneten Bedingungen mit Jod titriert werden. Der ursprüngliche Jodgehalt der Lösung kann in Kenntnis des Thiosulfatüberschusses bzw. des aus diesem gebildeten Tetrathionats berechnet werden.

Auch die Menge des Hypojodits lässt sich aus dem Unterschied zwischen dem in bekanntem Überschuss angewandten Thiosulfat und den Daten der Tetrathionat-Messung berechnen.

Da jedoch bei obiger Bestimmung das Äquivalentgewicht des Hypojodit-Jods das Vierfache des Atomgewichts des elementaren Jods beträgt (siehe Gl.7), verursacht ein eventueller Fehler bei der Titration eine bedeutende Abweichung. Es ist daher zweckmässiger, das beim Ansäuern eines getrennten Teils der Lösung freigewordene und das ursprünglich vorhandene Jod gemeinsam zu bestimmen und das Hypojodit aus der Differenz zu berechnen.

Bei Anwendung dieser Methode kann das ursprünglich vorhandene und das aus der Reduktion des Jods bzw. Hypojodits stammende Jodid in der gleichen Lösung nach entsprechender Verdünnung in Gegenwart von p-Äthoxychrysoidin als Adsorptionsindikator mit Silbernitratlösung direkt titriert werden.[11] Diese Methode wird nämlich durch die Gegenwart des Tetrathionats nicht gestört und so ist es nicht notwendig, einen dritten Anteil langwierig vorzubereiten.—Die zu befolgende Methode ist übrigens im Analysenschema Nr. 1. (siehe dort) kurz zusammengefasst.

Wenn die Lösung ausser relativ viel Jodid, Jod, Hypojodit auch Jodat enthält, d.h. wenn das Jod mit den Oxydationszahlen —I, 0, +I *und* +V *in seinen Verbindungen vorliegt*, so kann das Jodat nach der Titration des freien Jods und des Hypojodits, d.h. nach Rücktitration des Thiosulfatüberschusses bestimmt werden.† Die Lösung wird zu diesem Zweck angesäuert, und das in Freiheit gesetzte Jod mit Thiosulfat titriert.

Man kann auch vorgehen, indem man das bei letzterer Jodat–Jodid–Reaktion

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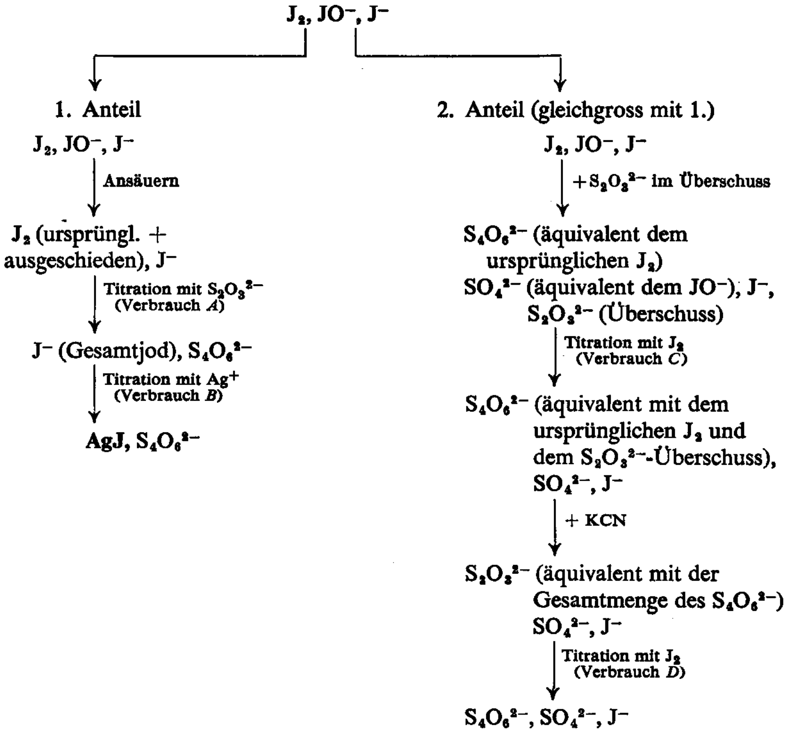
* Bei der Zugabe der Thiosulfatlösung findet eine geringgradige Änderung des pH-Wertes der Lösung statt, diese ist jedoch—da das System in allgemeinen gepuffert untersucht wurde—praktisch vernachlässigbar. Ist die zu untersuchende Lösung nicht gepuffert, muss die Thiosulfatlösung zuerst auf den pH-Wert der untersuchten Lösung eingestellt werden.

† Man darf dabei nicht vergessen, dass die Lösung oder die Thiosulfatlösung auf den pH-Wert der ursprünglichen Lösung gepuffert sein muss.



Analyseschema 1

gebildete Jod mit Sulfit bindet und nachher das Tetrathionat bestimmt. In solchen Fällen wird das Jodat in einem separaten Teil der Lösung bestimmt.

Bei dieser Methode hat sich (im Gegensatz zum vorangehenden Fall) Tetrathionat nur in der Reaktion des ursprünglichen Jods und des Thiosulfats sowie bei der Rücktitration des Thiosulfatüberschusses gebildet, da bei der Entfernung des aus dem Jodat gebildeten Jods (siehe Gl.3) nur das in dieser Hinsicht indifferente Sulfat entsteht:

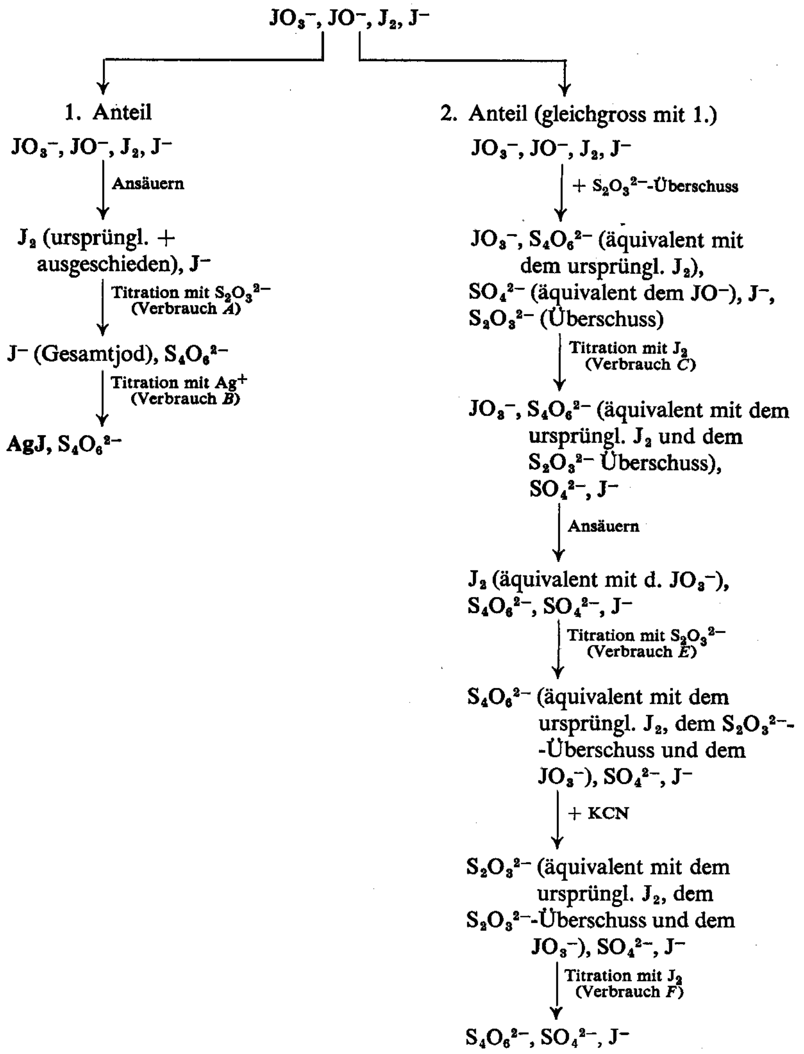
$$J_2 + SO_3^{2-} + H_2O = 2J^- + SO_4^{2-} + 2H^+ \qquad (9)$$

In diesem Falle wird das Jodat in einem getrennten Anteil der Lösung bestimmt, wobei durch Alkalischmachen auch das Jod zu Hypojodit umgesetzt und mit Phenol gebunden wird:[7]

$$J_2 + C_6H_5OH + OH^- = JC_6H_4OH + J^- + H_2O \qquad (10)$$

Wir möchten hierzu bemerken, dass das Jodat unter den gegebenen Umständen unverändert bleibt, und nach Ansäuern der Lösung jodometrisch bestimmt werden kann, da das elementare Jod in saurem Medium mit Phenol nicht mehr reagiert. Dieses Verfahren wird noch eingehender besprochen. Vorläufig verweisen wir auf die Analysenschemata 2 und 3.

Ein Jodid, Jod, Hypojodit, Jodat und Perjodat enthaltendes System (Jod mit den Oxydationszahlen —I, 0, +I, +V *und* +VII) *kann nur vorübergehend bestehen.* In diesem System reagiert das Perjodat im Gegensatz zu Jodat auch über pH = 8 mit Thiosulfat. Diese Reaktion ist jedoch keine eindeutige. Gleichfalls oxydiert das Perjodat—abweichend vom Jodat—das vorhandene Jodid bei ungefähr pH = 8 zu Jod



Analyseschema 2

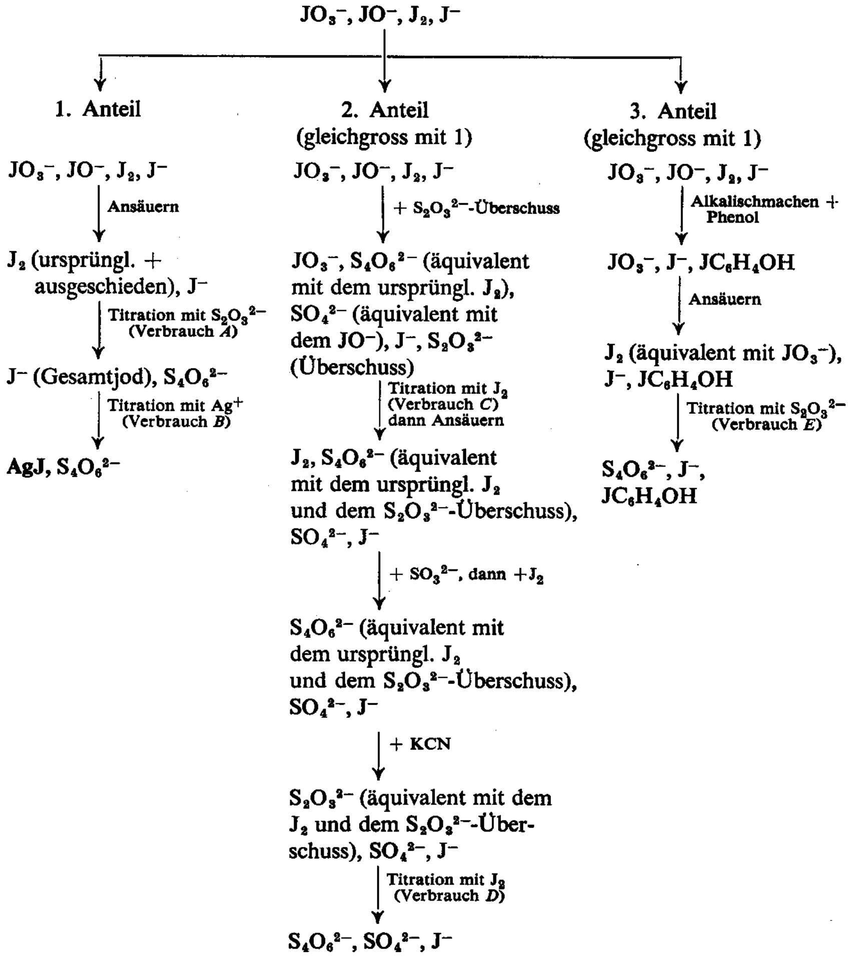
(seihe G1.4). Das Jod kann ausser den bereits erwähnten Ursachen auch deshalb mit Thiosulfat oder Arsenit nicht direkt titriert werden, weil die Perjodat–Jodid Reaktion eine Zeitreaktion ist. Während dieser Zeit geht im 0,01 n Massstabe eine nicht zu vernachlässigende Menge Jod bzw. Hypojodit in Jodat über. Mit Arsenit–Überschuss[12] kann jedoch durch Rücktitration mit Jod bei pH = 8 eine zufriedenstellende Genauigkeit erreicht werden.

Auch diese Methode beruht auf der Reaktion

$$JO_4^- + 2J^- + H_2O = JO_3^- + J_2 + 2OH^- \qquad (4)$$

da sie ja nur in Gegenwart von Jodid durchgeführt werden kann. Das vorhandene Arsenit reagiert jedoch sofort mit dem gebildeten Jod:

$$AsO_3^{3-} + J_2 + H_2O = AsO_4^{3-} + 2J^- + 2H^+ \qquad (11)$$

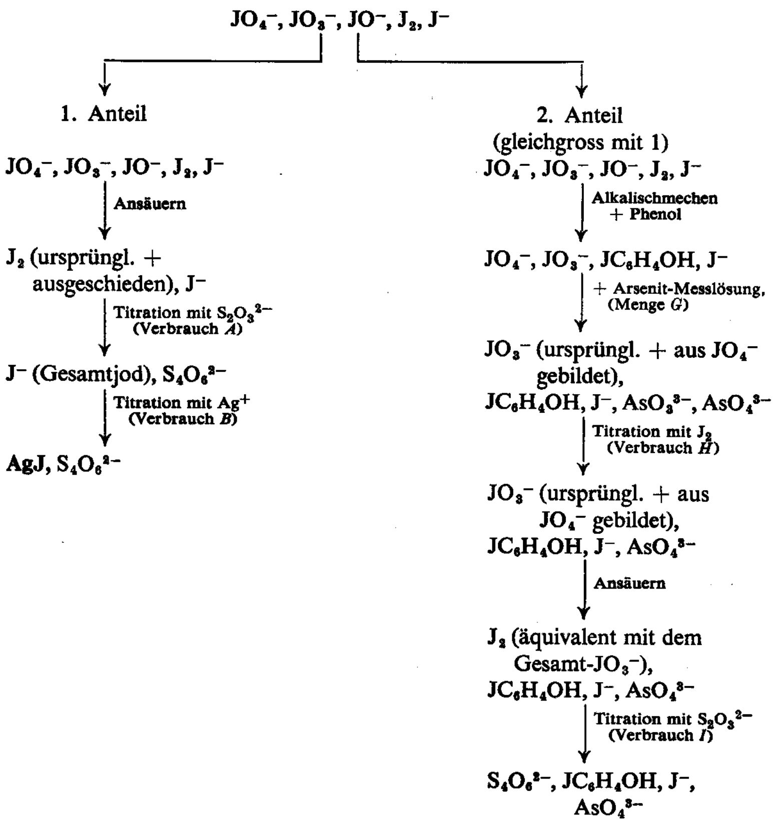


Analyseschema 3

Perjodat reagiert mit Phenol nicht, daher ist die Bestimmung des Perjodats auch in Gegenwart von Hypojodit (und Jod) möglich.

Diese Möglichkeit beruht gleichfalls auf der Ausnutzung der pH-Abhängigkeit der Reaktionsgeschwindigkeiten. Bei höheren pH-Werten läuft die Reaktion 4 nämlich langsam, der Prozess 10 jedoch augenblicklich ab. Bei Verminderung des pH-Wertes nimmt die Geschwindigkeit der Reaktion 4 allmählich zu, die der Reaktion 10 jedoch ab. Es erscheint hier aber allmählich auch der Prozess 11, der sich praktisch augenblicklich abspielt. Bei pH = 8 verschieben sich die Reaktionsgeschwindigkeiten noch mehr zugunsten der durch uns kontrollierbaren Reaktionen. Das in der Zeitreaktion 4 gebildete Jod reagiert nach der Gleichung 11 augenblicklich weiter, da die Reaktion zwischen Phenol und Jod bei pH = 8 bereits langsamer abläuft. Bei genügend rascher Vorbereitung ist also mit einem Perjodat–Verlust praktisch nicht zu rechnen.

Nach Titration des Arsenitüberschusses kann in der Lösung nach Ansäuern das ursprünglich vorhandene und das aus der Reduktion des Perjodats stammende Jodat jodometrisch bestimmt werden (siehe Analyseschema 4).



Analyseschema 4

Die Summe des Hypojodits und des elementaren Jods kann aus der jodometrischen Bestimmung der Gesamtmenge der oxydierenden Stoffe berechnet werden. Da das obenerwähnte System auch vorübergehend nur bei höheren pH-Werten bestehen kann, ist es zweckmässig, die Ergebnisse in Hypojodit–Jod anzugeben. Die getrennte Bestimmung der beiden Komponenten ist wegen der Perjodat–Thiosulfat Reaktion, nach den früher besprochenen Prinzipien nicht durchführbar.

Auf Grund unserer Untersuchungen wurde das in seinen Verbindungen in verschiedenen Oxydationszuständen vorliegende Jod nebeneinander nach weiter unten ausführlich beschriebenen Methoden bestimmt. Es muss ausdrücklich darauf hingewiesen werden, dass nach Abmessen der einzelnen Anteile der zu untersuchenden Lösung zuerst diejenigen Operationen auszuführen sind, welche die besonders labilen Gleichgewichte, bzw. der Verschiebung dieser vorbeugen. Diese Operationen sind das Hinzufügen von Phenol und Lauge (im Abschnitt II. bzw. III) das von Thiosulfat (im Abschnitt I. und II) endlich das Hinzufügen von Arsenit (im Abschnitt III). Wir möchten dabei vorausschicken, dass die nacheinanderfolgenden Operationen kontinuierlich, also ohne Unterbrechung der Reihe nach durchgeführt werden müssen, falls eine Wartezeit nicht ausdrücklich vorgeschrieben ist. Dies ist deshalb notwendig, weil bei einem Grossteil der Fälle die Differenzen zwischen den Reaktionsgeschwindigkeiten zu analytischen Zwecken ausgenützt werden.

TABELLE I. BESTIMMUNG VON PERJODAT, JODAT, HYPOJODIT, JOD UND JODID NEBENEINANDER

Nr.	Einwaage, *mg* (in Jod ausgedrückt)					Verbrauch, *ml*									Gefunden, *mg* (in Jod ausgedrückt)					Gesamtmenge Jod, *mg*	
	JO_4^-	JO_3^-	OJ^-	J_2	J^-	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	JO_4^-	JO_3^-	OJ^-	J_2	J^-	berechnet	gemessen
I	—	1,27	3,95	4,15	26,5	15,46	5,65	5,86	—	6,18	7,64	—	—	—	—	1,31	3,86	4,11	26,6	35,87	35,8
						15,44	5,62	5,70	—	6,08	7,53	—	—	—	—	1,28	3,85	4,16	26,4		35,6
						15,45	5,64	5,81	—	6,11	7,58	—	—	—	—	1,29	3,86	4,11	26,5		35,7
II	—	2,11	2,66	1,44	13,9	15,23	3,19	3,20	2,17	9,88	—	—	—	—	—	2,09	2,68	1,45	14,0	20,11	20,2
						15,23	3,17	3,15	2,14	9,90	—	—	—	—	—	2,09	2,68	1,43	13,9		20,1
						15,21	3,17	3,18	2,15	9,87	—	—	—	—	—	2,08	2,66	1,42	13,9		20,0
III	1,71	2,15	6,35	—	26,1	31,14	5,75	—	—	—	—	5,05	2,42	18,17	1,67	2,17	6,57	—	26,0	36,31	36,4
						31,13	5,73	—	—	—	—	5,05	2,40	18,21	1,68	2,17	6,56	—	25,9		36,3
						31,13	5,73	—	—	—	—	5,05	2,43	18,14	1,66	2,17	6,56	—	25,9		36,2

Zeichenerklarung:

A Verbrauch an 0,01 n Natriumthiosulfat Masslösung für alle oxydierenden Ionen
B Verbrauch an 0,05 n Silbernitratlösung für das gesamte Jodid nach Reduktion
C Nach Reduktion mit Natriumthiosulfat für den Überschuss bei pH = 8 verbrauchte 0,01 n Jodlösung
D Nach Reduktion des bei der vorangehenden Messung gebildeten Tetrathionats verbrauchte 0,01 n Jodlösung
E Für das Jodat verbrauchte 0,01 n Natriumthiosulfatlösung
F Nach Reduktion des bei den Titrationen *C* und *E*, sowie bei der Jod-Thiosulfat Reaktion gebildeten Tetrathionats verbrauchte 0,01 n Jodlösung
G Zugegebene Menge 0,01 n arsenige Säure
H Für den Überschuss der arsenigen Säure bei pH = 8 verbrauchte 0,01 n Jodlösung
I Für das ursprünglich vorhandene und bei der Reduktion des Perjodats gebildete Jodat verbrauchte 0,01 n Natriumthiosulfatlösung

Ein Teil unserer experimentellen Ergebnisse ist auch tabellarisch dargestellt. Die in der Rubrik "Einwaage, *mg*" der Tabelle angeführten Daten sind teils effektive Einwaagen, teils aus getrennten Messungen berechnete Werte, die auch auf Grund der Skrabalschen[1] Daten kontrolliert wurden. Die zu den Modellversuchen gebrauchte Lösung wurde aus drei Stammlösungen (0,01 n Perjodat-, Jodat-bzw. 0,01 n Jodid–Jod–Hypojodit–Lösungen) unmittelbar vor der Ausführung der Analyse vermengt. Die Mengenverhältnisse der Jodid–Jod–Hypojodit–Lösung müssten aus den Einwaagen auf Grund der Skrabalschen Daten rechnerisch ermittelt werden.

BESCHREIBUNG DER VERFAHREN

Reagenzien

Natriumthiosulfatlösung, 0,01 n
Kaliumjodidhaltige Jodlösung, 0,01 n
Arsentrioxydlösung (neutral), 0,01 n
Silbernitratlösung, 0,05 n
Kartoffelstärkelösung, 1 % ige mit 0,1 % Salicylsäure abgebaute und konservierte
p-Äthoxychrisoidinlösung, 0,2 % ige in 96 % igem Alkohol
Phenolphthaleinlösung, 0,1 % ige
Perchlorsäurelösung, 20 % ige
Kohlendioxyd (aus Stahlflasche)
Natriumhydroxydlösung, 20 % ige
Natriumhydroxydlösung, ca. 0,1 % ige
Kaliumcyanidlösung, 5 % ige
Phenollösung, 1 % ige
Formaldehydlösung, 5 % ige
Natriumsulfitlösung, 1 % ige
Die Reagenzien waren analytisch rein.

I. *Bestimmung von Jodid-Jod, elementarem Jod, Hypojodit- und Jodat-Jod, wenn relativ wenig Jodat und relativ viel Jodid vorhanden ist*

Ein genau gemessener 20–40 mg Gesamtjod entsprechender Anteil der zu untersuchenden Lösung wird in einem 100 ml fassenden Erlenmeyerkolben mit eingeschliffenem Glasstopfen mit so viel Perchlorsäure angesäuert, dass die Lösung auf Perchlorsäure etwa 0,1 normal ist. Nach 10 Minuten wird das ursprüngliche und das ausgeschiedene Jod in Gegenwart von Stärke als Indikator mit Thiosulfatlösung titriert. Die Zahl der verbrauchten ml 0,1 n $Na_2S_2O_3$ wird mit *A* bezeichnet.

Die austitrierte Lösung giesst man nun in einen geräumigeren Kolben, verdünnt auf ca. 200 ml und neutralisiert genau in Gegenwart von 1–2 Tropfen p-Äthoxychrysoidinlösung zuerst mit 20% iger Natronlauge, dann mit Perchlorsäure und schliesslich mit verdünnter Natronlauge. Es werden nun weitere 8–10 Tropfen p-Äthoxychrysoidinlösung zugegeben und das Jodid langsam und unter ständigem Rühren mit 0,05 n Silbernitratlösung titriert. Das p-Äthoxychrysoidin als Adsorptionsindikator schlägt im Endpunkt von himbeerrot auf gelb um. Der Verbrauch wird mit *B* bezeichnet.

In einem anderen, gleich grossen Anteil der Lösung lässt man nun rasch 1/2–1/6 des Volumens *A* der Thiosulfatlösung einlaufen. (Die notwendige Menge Thiosulfat wird nach der Menge Jodat, der relativen Menge Jod bzw. Hypojodit bemessen). Nach Vermischen werden 1–3 Tropfen Phenolphthaleinlösung zugegeben, dann wird so lange CO_2-Gas durch die Lösung geleitet, bis diese eben entfärbt ist und schliesslich in Gegenwart von 5–10 Tropfen Stärkelösung der Thiosulfatüberschuss mit Jodlösung titriert. Der Verbrauch wird mit *C* bezeichnet.

Man tropft nun Perchlorsäure zum Reaktionsgemisch bis das Brausen der Lösung nachlässt und dann noch so viel, bis der pH-Wert zwischen 1 und 2 liegt. Nach etwa 10 Minuten wird das ausgeschiedene Jod mit Thiosulfat titriert. Der dem Jodatgehalt proportionale Verbrauch wird mit *E* bezeichnet.

Die Lösung wird hierauf mit Natronlauge neutralisiert und noch 2 ml überschüssige Natronlauge, sowie 1–2 ml Kaliumcyanidlösung zugegeben. Man stellt die Lösung für 15 Minuten beiseite. Während dieser Zeit spielt sich die Reaktion 8 ab, dann werden zur Bindung des Cyanidüberschusses 1–2 ml Formaldehydlösung zugegeben. Nach einigen Minuten wird die Lösung schwach angesäuert und das gebildete Thiosulfat mit Jodlösung titriert. Der Verbrauch der Jodlösung wird mit F bezeichnet.

Die für die einzeilnen komponenten verbrauchten ml der Masslösungen können folgendermassen berechnet werden (siehe Analyseschema 2):

Der Verbrauch E ist unmittelbar dem Jodat-Jod proportional. Das Äquivalentgewicht ist im Sinne der Gleichung 3 ein Sechstel des Atomgewichts des Jodat-Jods.

Für das Jodat-Jod werden also E ml 0,01 n Thiosulfatlösung verbraucht.

Der ursprüngliche Jodgehalt kann aus dem Ergebnis der Tetrathionat-Titration (F) berechnet werden, unter Berücksichtigung dessen, dass in der Reaktion 8 aus einem Tetrathionat ein Thiosulfat gebildet wird (das Äquivalenzverhältnis ist also unterschiedliches von dem in der Reaktion 6), und dass sich sowohl bei der Thiosulfatmessung (C) als auch bei der Jodatmessung (E) Tetrathionat bildet.

Für das elementar vorhandene Jod werden also

$$[2F - (E + C)] = a$$

ml 0,01 n Thiosulfatlösung verbraucht. (Der Einfachheit halber wird dieser Wert mit a bezeichnet).

Das Äquivalentgewicht ist das Atomgewicht (siehe Gl. 6) des Jods.

Die Menge Hypojodit-Jods kann aus der für die Gesamtmenge des elementaren Jods bzw. der Jodverbindungen mit den Oxydationszahlen 0, +I, +V verbrauchten Messlösung (A) nach Abzug der für das Jodat und Jod verbrauchten Volumina berechnet werden.

Für das Hypojodit-Jod wurden also

$$[A - (E + a)] = b$$

0,01 n Thiosulfatlösung verbraucht.

Das Äquivalentgewicht des Hypojodit-Jods ist die Hälfte seines Atomgewichtes (siehe Gl. 1).

Schliesslich erhält man die ml der ursprünglichen Menge Jodid-Jod entsprechende Messlösung, wenn man aus dem Verbrauch B die ml Messlösung, welche zur Bestimmung des freien sowie des Hypojodit- bzw. Jodat-Jods verbrauchten Messlösung nach entsprechender Umrechnung, unter Berücksichtigung, dass die Silbernitratlösung 0.05 normal ist, in Abzug bringt.

Wenn man auf Grund der Reaktion

$$JO_3^- + 6e \rightarrow J^- \qquad (12)$$

die zur Bestimmung des Jodat-Jods verbrauchten ml Thiosulfatlösung in $AgNO_3$ Lösung umrechnen wünscht, so werden die ml Thiosulfatlösung mit 6 dividiert. So ist die Jodid-Jodäquivalente des aktuellen Jodat-Jods in 0,05 n $AgNO_3$ Masslösung ausgedrückt 1/30 = 0,0333.

Die zur Messung des elementar vorhandenen Jods verbrauchten ml 0,01 n Thiosulfatlösung werden schliesslich durch Multiplizieren mit 0,2 in 0,05 $AgNO_3$-Lösung umgerechnet, da die Jodmengen bei der jodometrischen und der beschriebenen argentometrischen Messungen äquivalent sind.

Dem Hypojodit-Jod äquivalente Menge Thiosulfatlösung ist im Sinne der Gleichung

$$JO^- + 2e \rightarrow J^- \qquad (13)$$

die Hälfte des tatsächlichen Masslösung-Verbrauches. Bei Umrechnung des letzteren in 0,05 n $AgNO_3$-Lösung muss demgemäss mit 0,1 multiplizieren.

Für den ursprünglichen Jodid-Jodgehalt wurde also $[B - (0{,}0333\,E + 0{,}2\,a + 0{,}1\,b)]$ ml 0,05 n $AgNO_3$-Lösung verbraucht.

Auf Grund obiger Darlegungen entspricht 1 ml 0,01 n Natriumthiosulfatlösung
0,2115 mg Jod im Oxydationszustand +V (Jodat);
0,6346 mg Jod im Oxydationszustand +I (Hypojodit); bzw.
1,2692 mg Jod im Oxydationszustand 0 (elementares Jod.)
1 ml 0,05 n Silbernitratlösung entspricht 6,346 mg Jod im Oxydationszustand −I (Jodid.)

II. *Bestimmung von Jodid-Jod, elementarem Jod, Hypojodit- und Jodat-Jod nebeneinander, wenn grössere Menge Jodat, und relativ viel Jodid vorhanden ist*

Im ersten Anteil der 20–40 mg Gesamtjod entsprechenden, genau eingemessenen Lösung werden die Menge des Jods im Oxydationszustand O, +I, +V und der gesamte Jodgehalt (letzterer in Form von Jodid) ebenso bestimmt wie bei der vorangehend im Abschnitt I. beschriebenen Methode. Die verbrauchten ml Masslösung werden auch hier mit A bzw. B bezeichnet.

Zum zweiten (gleich grossen) Anteil der Lösung wird gleichfalls ein Thiosulfatüberschuss zugegeben und der Überschuss bei pH = 8 mit Jodlösung titriert. Dieser Wert wird mit C bezeichnet.

Die Lösung wird nun angesäuert, und das gebildete Jod mit Sulfitlösung reduziert. Der Sulfitüberschuss wird mit 0,01 n Jodlösung gebunden. Man bestimmt hierauf den Tetrathionatgehalt der Lösung mit der bereits beschriebenen Cyanid-Methode. Der Verbrauch an 0,01 n Jodlösung wird mit D bezeichnet.

In einem dritten, gleich grossen aliquoten Teil wird schlieslich der Jodatgehalt nach folgender Methode bestimmt:

Man macht die Lösung mit 1 ml 20% iger Natronlauge alkalisch, und versetzt unverzüglich mit 1–2 ml Phenollösung. Nun wird auf 50 ml verdünnt und in Gegenwart von einigen Tropfen Phenolphthaleinlösung bis zur Entfärbung Kohlendioxyd eingeleitet. Man säuert hierauf mit so viel Perchlorsäure an, dass diese nicht nur die Hydrocarbonate zersetzt, sondern auch der Säuregehalt auf etwa 0,1 n eingestellt wird. Nach 10 Minuten wird die mit dem Jodat äquivalente Jodmenge mit Thiosulfat titriert. Der Verbrauch wird mit E bezeichnet. Der Gang der Analyse ist im Analyseschema 3 gezeigt.

Die für die einzelnen Komponenten verbrauchten Mengen der Masslösungen werden nach folgenden Formeln berechnet:

Für das Jodat: E ml;

für das Jod (da sich bei der Reduktion des Jodats kein Tetrathionat gebildet hat, siehe Gl. 9): $[2D - C] = c$ ml;

und für das Hypojodit (auf Grund der im ersten Kapitel beschriebenen Überlegungen): $[A - (E + c)] = d$ ml 0,01 n $Na_2S_2O_3$-Lösung.

Dem ursprünglichen Jodidgehalt der Lösung entspricht $[B - (0{,}0333\,E + 0{,}2\,c + 0{,}1\,d)]$ ml 0,05 n $AgNO_3$-Lösung.

Die Äquivalentgewichte sind die gleichen wie die im Abschnitt I angegeben worden sind.

III. *Bestimmung von Jodid-Jod, elementarem Jod, Hypojodit-, Jodat-, und Perjodat-Jod nebeneinander, wenn relativ viel Jodid-Jod verhanden ist*

Im ersten, 20–40 mg Gesamtjod entsprechenden, genau gemessenen aliquoten Teil werden die Messungen mit den Messwerten A bzw. B wie in den vorangehendenen Abschnitt II. bzw. I. durchgeführt.

Ein zweiter gleich grosser Lösungsanteil wird mit 1 ml 20% iger Natronlauge alkalisch gemacht und unverzüglich mit 1–2 ml Phenollösung, sowie mit einer genau gemessenen, dem erwarteten Perjodatgehalt entsprechenden Menge einer 0,01 normalen Lösung von arseniger Säure versetzt. Die Menge der arsenigen Säure wird mit G bezeichnet. Man gibt nun einige Tropfen Phenolphthalein hinzu und leitet bis zur Entfärbung CO_2 ein. Nach 15 Minuten wird der Überschuss der arsenigen Säure auf Stärke als Indikator mit 0,01 n Jodlösung titriert (H). Die Lösung wird auf etwa pH = 1 angesäuert und nach 15 Minuten wird das durch den ursprünglichen und den bei der Reduktion des Perjodats gebildeten Jodatgehalt freigemachte Jod mit 0,01 n Thiosulfatlösung titriert. Das Ergebnis wird mit I bezeichnet.

Für die einzelnen Komponenten wurden folgende Mengen Masslösung verbraucht:

Die Perjodatmenge kann in Kenntnis der Mengen der Arsenitlösung (C) und für deren Überschuss verbrauchten Jodlösung (H) berechnet werden.

Für das Perjodat wurden also

$[G - H] = e$ ml 0,01 n Thiosulfatlösung äquivalente 0,01 n arsenige Säure verbraucht.

Das Äquivalentgewicht des Perjodat-Jods ist auf Grund der Reaktion 4 die Hälfte des Atomgewichts. Im Laufe dieser Reaktion bildet sich Jodat, dies muss also bei der Berechnung der für das ursprüngliche Jodat verbrauchten Lösungsmenge berücksichtigt werden. Auch muss man in Betracht ziehen, dass zwischen den Reaktionen 3 und 4 ein Äquivalenz-Unterschied besteht, daher sind dem ursprünglichen Jodat-Jodgehalt der Lösung:

$[I - 3e] = f$ ml 0,01 n Thiosulfatlösung äquivalent.

Der gemeinsamen Menge Hypojodit + elementares Jod entsprechende ml Thiosulfatlösung erhält man, wenn man aus den dem elementaren + Hypojodit-, Jodat- und Perjodat-Jod anzeigenden ml A die für das Jodat- und Perjodat-Jod verbrauchten ml der Messlösung in Abzug bringt.

$$[A - (f + 4e)] = g \text{ ml}$$

Dem ursprünglichen Jodidgehalt der untersuchten Lösung (angenommen dass die Lösung nur Hypojodit nicht aber elementares Jod enthält und unter Berücksichtigung dessen, dass das Äquivalentgewicht des JO_4^- von dem auf Grund der Reaktion 4 berechneten auch hier abweicht) sind:

$[B - (0{,}1\,e + 0{,}0333\,f + 0{,}1\,g)]$ ml 0,05 n Silbernitratlösung gleichwertig.

Die Äquivalentgewichte für das Jod in verschiedenen Oxydationszuständen sind die gleichen die am Ende des Abschnittes I. angegeben worden sind bzw. 1 ml 0,01 n arsenige Säure entspricht (auf Grund der Reaktionen 4 und 11) 0,6346 mg Jod im Oxydationszustand + VII (Perjodat).

Schliesslich möchten wir noch erwähnen, dass unsere Untersuchungen mit solchen Systemen durchgeführt wurden, in denen die Menge Jodid–Jods im Verhältnis zum Jod mit anderen Oxydationszahlen im Überschuss vorlag. Ist wenig Jodid vorhanden, so muss vor den oxydimetrischen Titrationen eine entsprechende Jodidmenge in das System eingetragen werden. Das Jodid–Jod bzw. das Gesamtjod lässt sich in einem separat vorbereiteten (reduzierten)Lösungsanteil bestimmen.

Summary—A system consisting of iodide, iodine, hypo-iodite, iodate and periodate is labile, and has a transient existence at higher pH values. Periodate may be reduced, after decomposition of hypo-iodite, with phenol in an excess of arsenious acid, the excess of which is back-titrated. The iodate, after reduction of iodine and hypo-iodite by means of phenol, is determined iodometrically. In the presence of periodate, the quantity of iodate formed is equivalent to the periodate. The total quantity of hypo-iodite and iodine is calculated from the difference of the iodometric measurements (with and without phenol). After determination of the total amount of oxidising substance, the total amount of iodide can be measured with silver nitrate using *p*-ethoxychrysoidine as adsorption indicator. In the absence of periodate, elementary iodine along with hypo-iodite is determined using the same principles. Thiosulphate is oxidised by hypo-iodite to sulphate, but by iodine to tetrathionate. The latter can be determined by the procedure of Kurtenacker and Fritsch.

Résumé—Un système composé d'iodure, d'iode, d'hypoiodite, d'iodate et de periodate est labile et peut exister seulement aux fortes valeurs de pH sous contrôle. Certains auteurs réduisent le periodate, après décomposition de l'hypoiodite au moyen du phénol, avec un excès d'acide arsénieux, et titrent l'excès. L'iodate, après réduction de l'iode et de l'hypoiodite au moyen du phénol, est dosé par iodométrie. La quantité totale d'hypoiodite et d'iode est calculée d'après la différence des titres iodométriques (avec ou sans phénol). Après dosage de la quantité totale d'oxydant, l'iode total peut être dosé au moyen du nitrate d'argent, en utilisant la p-éthoxychrysoidine comme indicateur d'adsorption.

En l'absence de periodate, l'iode élémentaire en présence d'hypoiodite est dosé d'après le principe que le thiosulfate est oxydé en sulfate par l'hypoiodite, et en tétrathionate par l'iode. Cette dernière réaction peut être réalisée en utilisant le procédé de Kurtenacker et Fritsch. Les résultats sont satisfaisants.

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PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—III

ALUMINIUM

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Summary—A study has been made of the precipitation of aluminium from homogeneous solution with 8-acetoxyquinoline. The use of 8-acetoxyquinoline results in an aluminium precipitate with superior physical characteristics as compared to that produced in the conventional manner with 8-hydroxyquinoline. A separation of 25-mg quantities of aluminium from 300 mg of magnesium or 1000 mg of calcium can easily be made.

THE precipitation of aluminium from homogeneous solution as the 8-hydroxyquinolate was accomplished by Stumpf[1] who used urea to raise the pH of an acid solution containing urea and 8-hydroxyquinoline. 8-Acetoxyquinoline can also be used as a source of 8-hydroxyquinoline to precipitate metal 8-hydroxyquinolates from homogeneous solution.[2,3] The present paper describes the use of 8-acetoxyquinoline for the precipitation of aluminium in an acetate-buffered solution at pH 5.

PROCEDURE

Dissolve 1·0 g of 8-acetoxyquinoline in 25 ml of 1:1 acetic acid in a 250-ml beaker. Add immediately a solution containing 3 to 25 mg of aluminium and dilute to approximately 150 ml with distilled water. Adjust the pH slowly to 5·0 using filtered 1:1 ammonium hydroxide. Dilute the solution to 200 ml, cover the beaker with a watch-glass, and place on an electric hot-plate so regulated that the solution may be raised to approximately 50° and held at this temperature for 3 hr. Cool to room temperature and filter through a medium porosity filtering crucible, transferring and washing the precipitate with about 100 ml or less of cold water. Dry at 135 ± 5° for 1 hr and weigh as $Al(C_9H_6NO)_3$; the gravimetric factor is 0·0587.

REAGENTS

Aluminium: An aluminium solution was prepared by dissolving the high-purity metal (>99·9% aluminium) in hydrochloric acid and diluting. The standard value was obtained by precipitation of the aluminium with ammonium hydroxide.[4]

Calcium: Reagent grade $Ca(NO_3)_2 \cdot 4H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

Magnesium: Reagent grade $Mg(NO_3)_2 \cdot 6H_2O$ (General Chemical Company, New York).

8-*Hydroxyquinoline:* A solution was prepared by adding 5 ml of glacial acetic acid to 2·5 g of the reagent (Matheson, Coleman, and Bell Division of Matheson Company, East Rutherford, New Jersey); after warming to dissolve the reagent, the solution was diluted to 90 ml with warm water, cooled, filtered to remove solid matter, and then diluted to 100 ml.

8-*Acetoxyquinoline:* This reagent was prepared by the method of Salesin and Gordon[2] with slight modification, *i.e.*, instead of a 3-fold excess of acetic anhydride only a 20% excess was used.

EXPERIMENTAL

Preliminary investigations were made to determine the appropriate concentrations of reagents, the temperature of reaction, and the pH, which would result in the quantitative precipitation of aluminium 8-hydroxyquinolate in a form with desirable physical characteristics.

No precipitate could be obtained at pH 4·0, heating the solution, with 8-acetoxyquinoline present, for three hours at 45°. At pH 4·5, aluminium 8-hydroxyquinolate precipitated in the form of spherical aggregates at temperatures between 25 and 75°; above 75° the physical appearance of the precipitate began to change and stubby needles, with slight curvature, were formed between 85° and the boiling

TABLE I.—SEPARATION AND DETERMINATION OF ALUMINIUM BY PRECIPITATION AS THE 8-HYDROXYQUINOLATE

Number	1	2	3	4	5	6	7	8	9	10
Method of precipitation	Conventional	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS
Modifications in precipitation procedure	a	b c	b	b	d	d	d	d	d	d
Diverse element taken, *mg*	none	none	none	none	none	none	none	Mg 100	Mg 300	Ca 1000
Aluminium taken, *mg*	25·67	25·67	10·27	25·67	3·08	10·27	25·67	25·67	25·67	25·67
Difference, *mg*	−0·11 −0·01 +0·01	−0·19 −0·16 −0·18	−0·07 −0·06 −0·02 −0·03 −0·03	0·00 +0·02 0·00	+0·10 +0·10 +0·01	+0·03 −0·02 −0·03	+0·02 +0·05 +0·03 +0·01 +0·02 +0·07 +0·06	+0·09 +0·05 +0·08	+0·11 +0·05 +0·10	+0·01 +0·06 +0·03

a. Aluminium precipitated by the method of Knowles.[7]
b. The initial pH of the solution was 4·5.
c. Transfer of the precipitate was made with filtrate as described by Takiyama *et al.*[3]; 0·8 g of 8-acetoxyquinoline used instead of customary 1-g amount.
d. The initial pH of the solution was 5·0.

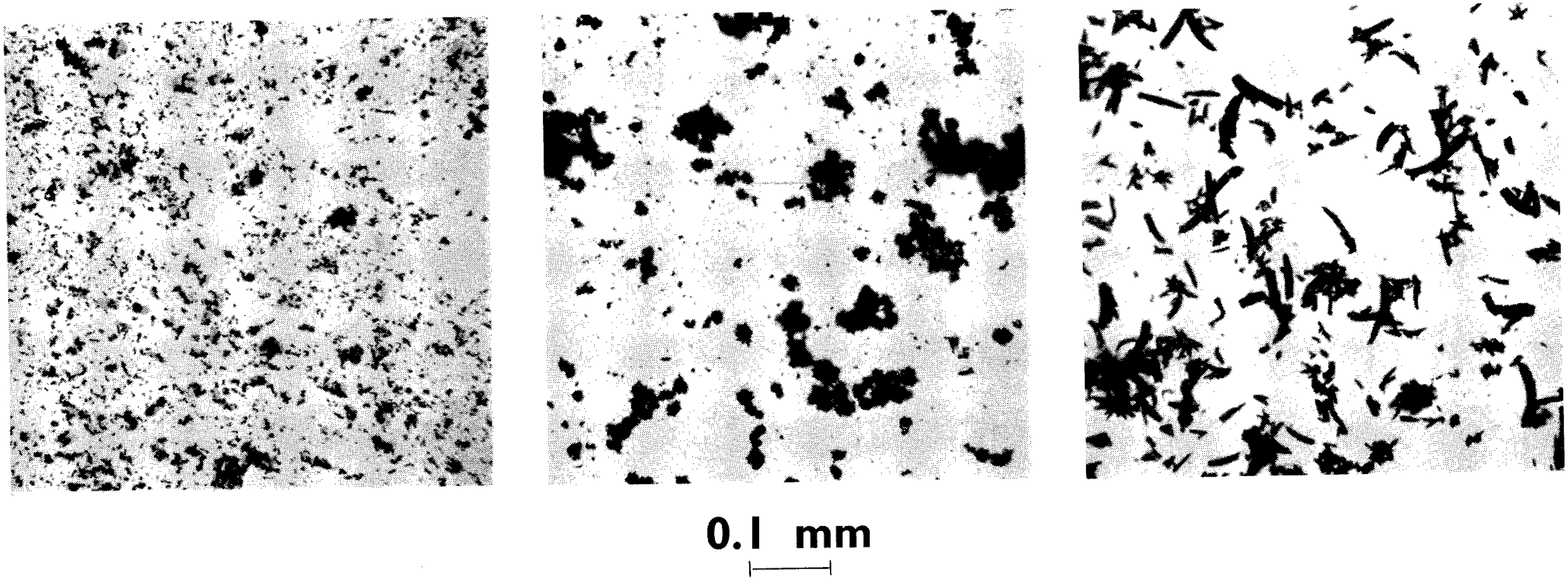

FIG. 1.—Photomicrographs of aluminium 8-hydroxyquinolate (all photomicrographs are at same magnification)

a, left panel: conventional method of precipitation.
b, centre panel: prepared by PFHS as described in procedure (t = 50°).
c, right panel: prepared by PFHS as described in procedure, but at boiling temperature.

point. In all cases the precipitate was of better physical form than that obtained by a direct method of addition of 8-hydroxyquinoline. Only spherical aggregates were obtained within the pH range 4·5 to 8·0, at 25 to 45°. Above pH 7·8, precipitation of the aluminium with 8-acetoxyquinoline occurred almost instantly.

The best results for analytical purposes were obtained by using 1·0 g of 8-acetoxyquinoline (approximately twice the stoichiometric quantity required for 25 mg of aluminium), heating the solution for 3 hr at 50°, and buffering at a pH of 5·0. Almost equally satisfactory results were obtained at pH 4·5.

Photomicrographs of several aluminium 8-hydroxyquinolate precipitates are shown in Fig. 1.

RESULTS AND DISCUSSION

Table I shows that satisfactory results can be obtained with from 3 to 25 mg of aluminium using the procedure given. Results obtained at pH 4·5 are also given although they appear to be slightly low in some cases.

With an initial pH of 5·0, the buffer capacity of the solution is such that the final pH will not vary more than ±0·2 pH unit.

Spectrophotometric determination of the aluminium[5] in the filtrate and wash showed that the combined solubility loss is quite small, *i.e.*, less than 0·02 mg.

According to Goto,[6] calcium begins to precipitate at pH 6·11 and magnesium at pH 6·7 so that a good separation of aluminium from calcium and magnesium can be expected. The results of Table I show that 25 mg of aluminium can easily be separated from at least up to 1000 mg of calcium and up to 300 mg of magnesium.

Acknowledgment—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation reported herein under Contract AT(11-1)-582 and of the Case Research Fund.

Zusammenfassung—Eine Studie der Fällung von Aluminium mit 8-Acetoxychinolin aus homogener Lösung wurde durchgeführt. Die Niederschläge zeigen erheblich bessere physikalische Eigenschaften, als Fällungen, die mit Oxin erhalten wurden. 25 mg Aluminium können leicht von 300 mg Magnesium und 1000 mg Calcium getrennt werden.

Résumé—Les auteurs ont étudié la précipitation de l'aluminium par la 8-acétoxyquinoléine en solution homogène. La 8-acétoxyquinoléine est utilisée, car le précipité d'aluminium a des caractéristiques physiques supérieures à celles obtenues dans la méthode ordinaire avec la 8-hydroxyquinoléine. Une séparation de 25 mg. d'aluminium d'une part, et de 300 mg. de magnésium ou 1000 mg. de calcium d'autre part peut facilement être réalisée.

Authors' Note: During the time that the present investigation was being completed, Howick and Trigg also reported on the precipitation of aluminium from homogeneous solution with 8-acetoxyquinoline, at the American Chemical Society meeting, New York, September 11–16, 1960. These authors also reported a method of synthesis of 8-acetoxyquinoline which differs in several respects from that described previously by Salesin and Gordon.[2] Although the latter paper, published in March 1960, mentions the precipitation of aluminium with 8-acetoxyquinoline, consultation between one of us (L.G.) and Professor Howick indicates that both investigations were independently conceived.

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ISOTOPIC DILUTION ANALYSIS BY SOLVENT EXTRACTION—II

HIGHLY SELECTIVE DETERMINATION OF ZINC WITH DITHIZONE

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Summary—Zinc has been determined by a single extraction in the form of a complex with dithizone, in amounts of the order of 10^{-6} to 10^{-8} g/ml with an average precision of $\pm 1{\cdot}0\%$, and in amounts of the order of 10^{-9} g/ml with an average precision of $\pm 15\%$. In the analysis even a large excess of metals which form extractable complexes with dithizone does not interfere. The method is very simple and rapid, for it consists of a single extraction of the solution to be analysed and measurement of the activity of the extract obtained. The procedure developed is more precise and sensitive than the colorimetric determination of zinc with dithizone.

INTRODUCTION

In a preceding paper[1] the theoretical foundation was given for the determination of trace amounts of metals by extraction followed by isotopic dilution analysis. From this work it was concluded that in each case an element may be selectively determined, in the form of an extractable complex, which has the highest value of the constant of the extraction process, K. The selective determination of such an element does not present any great difficulties. To prove the possibility of using this method under more difficult conditions the determination of zinc has been chosen, because in this case a masking agent must be used to attain selectivity.[1] The determination of trace amounts of zinc is also important from a practical point of view in ascertaining the purity of semi-conductor materials.

EXPERIMENTAL

Apparatus

A scintillation counter with well-type NaI(Tl) crystal.

A pH-meter Radiometer TTT1 (Copenhagen).

A mechanical shaker, glass test-tubes with ground stopper, volume 25 ml.

Reagents

Distilled water: Twice-distilled, free from zinc. Purity was controlled by a colour reaction with dithizone.

Carbon tetrachloride: A.R., twice distilled.

Dithizone: A.R.

Buffer solution: $0{\cdot}1N$ ammonium chloride was purified twice by dithizone and its pH regulated by the addition of ammonia, purified twice by isothermal distillation.

Hydrochloric acid: A.R., purified by repeated distillation.

Diethanoldithiocarbamate:[2,3] Prepared by mixing 6·0 g of A.R. diethanolamine and 3·5 g of A.R. carbon disulphide in 120 ml of absolute A.R. methanol. Before each experiment 50 ml of this solution was mixed with 450 ml of ammonium chloride—ammonia buffer and purified by dithizone extraction to remove the last traces of zinc [solution (I)].

Radio-zinc solution (^{65}Zn, $T_{1/2} = 250$ days):[4] A solution of specific activity 100 mc/g of zinc was always diluted to the necessary concentration with twice-distilled water. A solution of non-active zinc was prepared by dissolving 99·999% pure metal in the necessary amount of sulphuric acid and was diluted to the required concentration by twice-distilled water.

Procedure

To 10 ml of the analysed solution of non-active zinc (of the order of magnitude of 10^{-6} g of zinc/ml), which contained a great excess of other metals, 42·50 × 10^{-6} g of radio-zinc (y) were added. After the addition of 4 ml of solution (I) the pH of the analysed solution must reach a value of 7·5 to 8·5. If the original solution is too acid, its acidity must be decreased with ammonia free from zinc. The solution thus prepared is extracted by about 1·4 ml of 10^{-4} M dithizone solution in carbon tetrachloride. After shaking for 20 min, the organic phase is separated and the activity of 1·00 ml of the solution is measured by a scintillation counter (A_2). At the same time a solution, containing (40–100) × 10^{-6} g of radio-zinc, 4 ml of solution (I) and 1·4 ml of the same amount of dithizone solution in carbon tetrachloride, is extracted. The activity of 1·00 ml of the extract is measured by a scintillation counter (A_1). The amount of non-active zinc determined is calculated from the relation:

$$x = y\left(\frac{A_1}{A_2} - 1\right).$$

RESULTS AND DISCUSSION

In Table I the results are given of determinations carried out by the procedure described, and the errors are evaluated for the various concentration regions. At the

TABLE I.—EXTRACTION OF ZINC BY DITHIZONE
(3·2 × 10^{-6} g of Zn/ml to 3·2 × 10^{-9} g of Zn/ml[a])

Zinc taken, μg (X)	Active zinc added, μg (y)	Activity of extracts[b]		Zinc found, μg (x)	Deviation from mean, μg (Δ)	Other metals present, μg	Deviations[c]
		A_1	A_2				
32·65	42·50	79·788	44·994	32·90	+0·51	0	σ = 32·39
		79·402	45·206	32·16	−0·23	1000 Cu^{2+}	δ = ±0·174 = ±0·54%
		79·402	45·048	32·41	+0·06	1000 Hg^{2+}	σ − X = −0·26 = −0·8%
		79·402	45·217	32·11	−0·28	500 Fe^{2+}	
		81·068	45·674	32·96	+0·57	1000 Co^{2+}	
		81·068	45·626	33·08	+0·69	500 Cu^{2+}	
		81·410	46·918	31·30	−1·09	500 Sn^{2+}	
		81·410	46·404	32·10	−0·29	1000 Bi^{3+}	
		81·410	46·109	32·56	−0·17	1000 Pb^{2+}	
		79·518	45·524	31·70	−0·69	0	
		79·518	44·777	32·00	+0·59	0	
3·265	4·250	47·909	26·846	3·345	+0·026	100 Pt^{4+}	σ = 3·319
		47·909	26·654	3·331	+0·012	100 Cu^{2+}	δ = ±0·003 = ±0·9%
		46·476	25·842	3·388	+0·069	500 Ni^{2+}	σ − X = +0·051 = +1·8%
		46·476	26·160	3·300	−0·019	300 Cu^{2+}	
		43·857	24·691	3·300	−0·019	100 Co^{2+}	
		49·239	27·082	3·469	−0·150	500 Hg^{2+}	
		49·239	28·081	3·216	−0·103	500 Cd^{2+}	
		49·239	28·298	3·150	−0·169	500 Pb^{2+}	
		46·476	25·885	3·380	+0·061	1000 Cu^{2+}	
0·3265	0·4250	64·000	37·000	0·3108	−0·0235	50 Ag^{1+}	σ = 0·3343
		64·000	35·100	0·3503	+0·0160	50 Bi^{3+}	δ = ±0·00523 = ±1·57%
		64·000	36·270	0·3250	−0·0093	50 Fe^{2+}	σ − X = +0·0078 = +2·4%
		64·000	36·440	0·3210	−0·0133	50 As^{3+}	
		32·570	18·225	0·3340	−0·0003	50 Cd^{2+}	
		24·951	13·990	0·3366	+0·0023	50 Pb^{2+}	
		24·951	13·740	0·3469	+0·0126	50 Cu^{2+}	
		23·600	12·930	0·3501	+0·0158	50 Hg^{2+}	
0·03265	0·2125	7·880	7·020	0·0269	−0·0134	5 Ni^{2+}	σ = 0·0403
		7·880	7·100	0·0234	−0·0169	5 Cu^{2+}	δ = ±0·0061 = ±15·2%
		7·470	6·400	0·0353	−0·0050	10 Co^{2+}	σ − X = 0·0077 = +19%
		7·470	5·870	0·0580	+0·0177	10 Hg^{2+}	
		7·470	5·865	0·0580	+0·0177	0	

[a] Volume of analysed solution in all experiments listed in Table was 10 ml.
[b] In the range 3 × 10^{-6} g of Zn/ml, CHA = 1 × 10^{-4} M and A_1, A_2 expressed in cpm.
3 × 10^{-7} g of Zn/ml, CHA = 5 × 10^{-5} M and A_1, A_2 expressed in cpm.
3 × 10^{-8} g of Zn/ml, CHA = 0·5 to 1·0 × 10^{-5} M and A_1, A_2 expressed in cp 5 min.
3 × 10^{-9} g of Zn/ml, CHA = 2 × 10^{-6} M and $A_{,1}$ A_2 expressed in cp 5 min.

[c] $$\sigma = \frac{\sum_{x=1}^{x=n} X}{n}, \qquad \delta = \pm\sqrt{\frac{\Sigma\Delta^2}{n(n-1)}}$$

same time the amounts of added active zinc and dithizone concentrations c_{HA} are given. The dithizone concentration is always lower than would correspond to the stoichiometric amount of zinc present.

The influence of pH on the extraction of zinc by a 10^{-4} *M* solution of dithizone in carbon tetrachloride is shown in Fig. 1. In these experiments the volume of the aqueous phase was ten times larger than the volume of the organic phase, so that zinc was present in excess with respect to dithizone. Under these conditions, at pH 7·0 to 9·5 the maximum amount of zinc is extracted, which is in agreement with the predicted value.[1] In this region the influence of pH on the extraction of zinc is negligible.

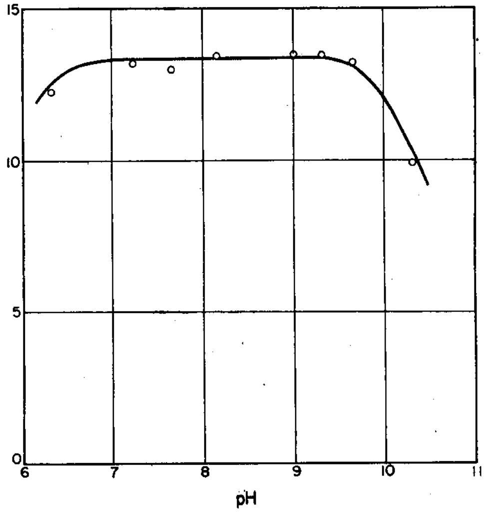

Fig. 1.—Influence of pH on the amount of extracted zinc-dithizonate (^{65}Zn labelled) in CCl_4. Activity, *A*, is expressed in 10^3 cpm.

By studying the influence of the time of shaking on the extraction of zinc it was found that in the pH region 7·0 to 9·5 equilibrium had already been attained after shaking for 10 min.

From Table I it is seen that by the proposed method it is possible to determine amounts of zinc of the order of 3×10^{-6} to 3×10^{-8} g/ml with an average precision of ±1%. In the region of 3×10^{-9} g of zinc/ml the precision was substantially lower (±15%). The increase of the mean deviation of the arithmetic mean of a number of measurements,

$$\delta = \pm\sqrt{\frac{\Sigma\Delta^2}{n(n-1)}},$$

with a decreasing concentration of determined zinc is caused in part by a decrease of the measured activity, and in part by the fact that the elution of zinc from the material of the vessels employed influenced more and more the precision of the analysis. This is also to be seen from the fact that the amount of zinc found at the lowest concentrations was a little higher than the amount of zinc added. The substantial increase of the error in the analysis of the smallest amounts of zinc was caused above all by the fact that the low specific activity of the employed radio-zinc necessitated, at this concentration, dilution with the analysed solution of non-active zinc in a ratio of 5:1. The variation of the measured activity at low count rates of 1800 cpm and high background of 600 cpm already greatly influenced the result of the analysis.

The presence of metals having a value of *K* lower than the *K* value of zinc dithizonate interferes in the determination of zinc.[1] To eliminate the influence of these cations various methods were examined. Firstly, the precipitation of interfering metals with hydrogen sulphide in an acidic medium was tried. This method was not successful, because the precipitate of sulphides formed contained nearly all of the zinc. The elimination of interfering elements by electrolysis was also unsuitable. In using thiosulphate as a masking agent, excess cadmium, cobalt and nickel interfered. The influence of interfering ions is best eliminated with diethanoldithiocarbamate. This reagent was chosen on the basis of the work of Margerum and Santacana[3] and proved successful. Diethanoldithiocarbamate forms crystalline precipitates with interfering metals, which do not adsorb traces of zinc on their surface, so that it is possible to add the reagent directly to the extracted solution. From Table I it is evident that in the determination of zinc in the presence of diethanoldithiocarbamate there is no interference even from a multifold excess of metals capable of extraction by dithizone: mercury, silver, platinum^{IV}, copper, bismuth, cadmium, cobalt, nickel, iron, lead and tin.

The proposed method is very simple and rapid. A single extraction of zinc from a solution containing an excess of interfering metals is far simpler than the conventional colorimetric determination of zinc by dithizone. From a comparison of our results with data from the literature[5] it is evident that determination of zinc by this method is far more sensitive than determination by activation analysis, spectral analysis, amperometry or flame photometry and more sensitive than colorimetric determination of zinc. This sensitivity could be further increased by the use of radio-zinc of higher specific activity. The method of isotopic dilution has the further advantage, that after the isotopes have been mixed there may be further losses of the element determined, in subsequent operations (for instance in separating the solution from the suspension in the analysis of samples), without endangering the result of the analysis.

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Zusammenfassung—Zink wurde bestimmt in Mengen von 10^{-6}–10^{-8} gZn/ml unter Anwendung einer einzigen Extraktion des Dithizonkomplexes. Die Genauigkeit beträgt 0,1%. Selbst 10^{-9} g Zn/ml können bestimmt werden, doch ist die Genauigkeit nur mehr 15%. In der Analyse stören selbst grosse Mengen von Metallen nicht, die ebenfalls Dithizonkomplexe bilden. Die Methode ist einfach und schnell, efordert eine einzige Extraktion und Zählung der Radioaktivität im Extrakt und ist genauer als die kolorimetrische Bestimmung mit dem selben Reagens.

Résumé—Le zinc a été dosé par simple extraction sous forms d'un complexe avec la dithizone: des quantités de 10^{-6} à 10^{-8} g de Zn/ml avec une précision moyenne de ±0,1% et des quantités de 10^{-9} g de Zn/ml avec une précision moyenne de ±15%. Même un grand excès de métaux qui forment des complexes extractibles par la dithizone ne gêne pas l'analyse. La méthode est très simple et rapide; elle consiste en une extraction simple de la solution à analyser et en une mesure de la radioactivité du corps extrait. La méthode est plus sensible et plus précise que le dosage colorimétrique du zinc par la dithizone.

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DETERMINATION OF TRACES OF TELLURIUM

BISMUTHIOL II AS A REAGENT FOR TELLURIUM

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Summary—A spectrophotometric study of the new tellurium bismuthiol II reaction has been made to ascertain its suitability for the determination of traces of tellurium. The reaction mechanism is discussed. The yellow tellurium compound which is developed at pH 2·0–2·2 is stable, and is quantitatively extracted by chloroform at pH > 5. Addition of ammonium sulphate increases the rate of extraction. Two procedures, using aqueous solution with an absorption maximum at 395mμ, or solvent extraction with an absorption maximum at 335 mμ, are proposed. The extraction procedure makes the method more selective and sensitive. Many common ions do not interfere when EDTA and citrate are used as masking agents. The interferences from mercury, iron, copper, and selenium are serious. Beryllium or selenium may be used as collecting agents in the presence of EDTA for separation of tellurium. Selenium may subsequently be removed by volatilisation with bromine and hydrobromic acid. The absorptivity and sensitivity of the reaction were found to be 28,000 and 0·005 μg tellurium per cm^2, respectively, at 335 mμ.

INTRODUCTION

Bismuthiol II (5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione) has been used for the determination of bismuth, palladium, and other metals.[5,9,10,12] This reagent has not been used for the determination of selenium or tellurium.* It was found that it reacts with selenium or tellurium below pH 5 forming a yellow coloration or precipitate which can be extracted by chloroform. A very sensitive and highly selective method for selenium is already available,[3] and therefore no attempt was made to utilise this reagent for selenium. However, a sensitive, selective, and satisfactory method for tellurium is still lacking; hence, an investigation aimed at utilisation of this reagent for determining traces of tellurium was undertaken.

Two sensitive methods for tellurium are available: (*a*) the iodide method of Johnson and Kwan[6] and (*b*) the dithiocarbamate method of Bode.[1,8] In the first method, the complex cannot be extracted by organic solvents and is subject to many interferences; in the second method the complex can be extracted by organic solvents and is more selective than other known methods for tellurium. But both methods are very sensitive to light, especially ultraviolet light. This is a serious drawback, since their absorption maxima are in the ultraviolet or near ultraviolet region. Not only is the colour reaction of the bismuthiol II method sensitive for traces of tellurium, but also the colour is stable. The variables for development and extraction of the coloured product have been studied. The precision of the method was found to be within ±2%.

QUALITATIVE TEST

Bismuthiol II reacts with many metals forming coloured products in acidic or alkaline medium.[5,9,10,12] The selectivity due to the masking action of EDTA at various pH values has been reported.[4] Iron, copper, palladium, silver, gold, cadmium, mercury,

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* After this paper was presented for publication, a paper appeared on the photometric determination of tellurium with bismuthiol II, J. Jankovský and O. Kšir, *Talanta*, 1960, **5**, 238.

thallium, lead, arsenic, antimony, bismuth, selenium, and tellurium still react with bismuthiol II in the presence of EDTA (ethylenediaminetetraacetic acid) and tartrate or citrate, but none of these, except silver, mercury, gold, and thallium, react at pH > 6. When cyanide is also added as a masking agent, at pH above 6, the reaction for thallium is highly selective. All platinum metals react with the reagent in the presence of EDTA, but above pH 10, only rhodium and iridium react in the presence of EDTA. At pH 2·2, cyanide does not effectively mask copper. Cerium^{IV} gives a white precipitate with bismuthiol II in the presence of EDTA at pH $< 2{\cdot}5$, probably due to oxidation.

PROPERTIES OF THE REAGENT AND ITS TELLURIUM COMPOUND

Bismuthiol II in the form of the acid or its potassium salt is pure white, changing to yellow when exposed to air. The potassium salt is soluble in water and stable, and its 1% aqueous solution is almost colourless. Its solubility in organic solvents depends on pH, as the acid form is in general more soluble in the organic solvent.

With tellurium or selenium it forms an intense yellow-coloured compound or precipitate in acidic medium below pH 5, but the compound is decomposed above pH 8. The compound is extracted at pH 5–8 by alchohols, ketones, chloroform or carbon tetrachloride. The compound is stable in both aqueous solution and organic solvents. The reagent is oxidised, probably to disulphide, by many strong oxidising agents such as persulphate, ferricyanide, *etc.* The reaction with tellurium or selenium goes to completion relatively slowly.

The tellurium or selenium bismuthiol II precipitate is sensitive to high temperature; it changes from yellow to brick red at a temperature above 50°. It can be dried at room temperature under vacuum to a constant weight. Addition of methanol, ethanol, or acetone to the freshly prepared precipitate liberates elemental tellurium (see Table I). Bismuthiol I (2,5-dimercapto-1,3,4-thiodiazole) reacts in a similar manner with selenium, tellurium, iron^{III}, copper, and other elements. However, when the yellow precipitate of tellurium (or selenium) bismuthiol I is dissolved by addition of ammonium hydroxide, elemental tellurium (or selenium) is precipitated. With bismuthiol II, the yellow selenium precipitate is more difficultly dissolved than the yellow tellurium precipitate. Upon addition of ammonium hydroxide, furthermore, neither elemental selenium nor elemental tellurium is immediately precipitated. This reduction reaction differentiates bismuthiol I from bismuthiol II.

TABLE I.—REACTION OF ORGANIC SOLVENTS

Bismuthiol II precipitate	pH	Methanol	Ethanol	Acetone
Se	2·2	—	—	*
	6·8	—	**	**
Te	2·2	—	—	+
	6·8	+	+	+

— No apparent effect.
+ Elemental tellurium separated, and the solution became dark.
* The precipitate dissolved to give a light yellow solution.
** Elemental selenium separated, and the solution showed a tan to reddish turbidity.

EXPERIMENTAL

Reagents and Apparatus

Bismuthiol II (potassium salt of 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione): 1% aqueous solution.

Citric acid: 1*M*.

Ammonium sulphate: 50% w/v aqueous solution, adjusted to pH 2·2 with sulphuric acid.

EDTA (sodium salt of ethylenediaminetetra-acetic acid): 0·1*M*.

Standard tellurium solution: Dissolve 0·1 g of pure tellurium in 5 ml of concentrated sulphuric acid by heating. Fume to drive off most of the acid. After cooling, carefully add 100 ml of water and dissolve the tellurous acid precipitate by adding a minimum amount of 4*M* potassium hydroxide solution, then making to 1 litre. This solution contains 0·1 mg of tellurium per ml. More dilute solutions may be prepared by appropriate dilution from the stock solution.

Polyvinyl alcohol: 2% aqueous solution.

Other reagents are analytical reagent grade.

Beckman spectrophotometer Model DU and *Beckman pH meter Model G* or equivalent.

Procedure

Preparation of calibration curves

(*a*) *Aqueous Solution.* Transfer 0, 1·0, 2·0, 3·0, 4·0, and 5·0 ml of standard tellurium solution (25 μg of tellurium per ml) to 125-ml beakers. Add 1 ml of 1*M* citric acid and 1 ml of 2% polyvinyl alcohol solution, dilute with water to approximately 15 ml, add 2 ml of bismuthiol II solution, and set aside for 20–30 min. Adjust the pH to 6·5 carefully with 6*M* ammonium hydroxide, while stirring. Transfer to 25-ml volumetric flasks and make to volume. While stirring or mixing avoid the formation of foams. Measure the absorbance at 395 mμ using a reagent blank.

(*b*) *Solvent Extraction.* Transfer 0, 1·0, 2·0, 3·0, 4·0, and 5·0 ml of the standard tellurium solution (10 μg tellurium per ml) to 125-ml beakers, add 6 ml of ammonium sulphate solution, and dilute to approximately 25 ml. Add 1 ml of 1*M* citric acid solution, 3 ml of 1% bismuthiol II solution, and set aside for 20–30 min. Adjust the pH to 6·5 with 6*M* ammonium hydroxide. Transfer to 125-ml separatory funnels. Shake vigorously with 10·0 ml of chloroform for 1 min. After filtering through glass wool, measure the absorbance at 335 mμ, using a reagent blank.

The conditions, the volume of the solution, the pH, *etc.* should be carefully controlled in order to obtain good reproducibility.

DISCUSSION AND RESULTS

Spectral characteristics

The absorbance curves for the bismuthiol II and the tellurium compound in aqueous solution and in chloroform are shown in Figs. 1 and 2. The curves indicate

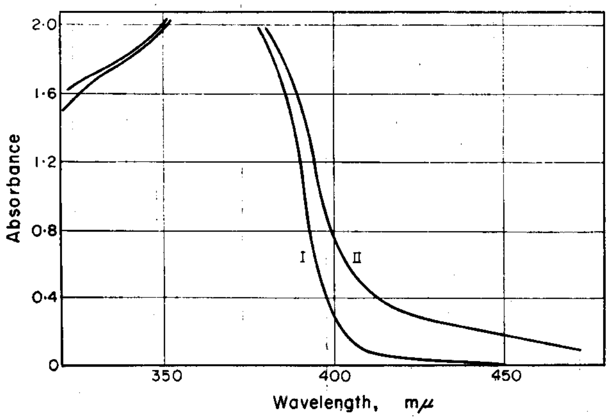

FIG. 1.—Absorption spectra, aqueous solution. (pH = 6·2: water as blank.)
I—Bismuthiol II.
II—40 μg Te + bismuthiol II in 10 ml of aqueous solution.

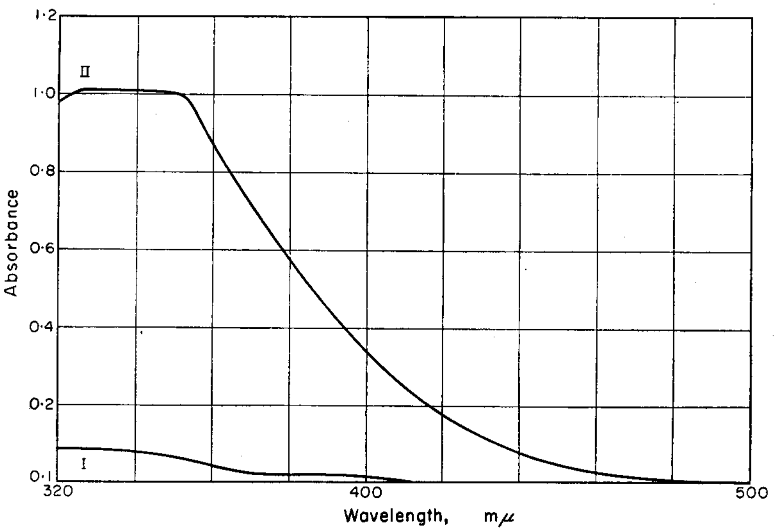

FIG. 2.—Absorption spectra, chloroform solution. (pH = 6·2 for extraction; chloroform as blank.)
I—Bismuthiol II in chloroform.
II—40 μg Te + bismuthiol II in 10 ml of chloroform.

that the tellurium compound in aqueous solution has an absorption maximum at 395–400 mμ, and in chloroform has an absorption maximum at 335–340 mμ. Since a small amount of bismuthiol II is also extracted by chloroform, a reagent blank should always be used when the chloroform extract is measured below 400 mμ.

Effect of reagents

It was found satisfactory to use 2 ml of 0·1 % bismuthiol II solution in aqueous solution and 3 ml in the solvent extraction procedure (Fig. 3). When EDTA is added for masking purposes, the actual amount of EDTA required depends upon the amounts of interfering metals present. The amount of EDTA has no effect on the

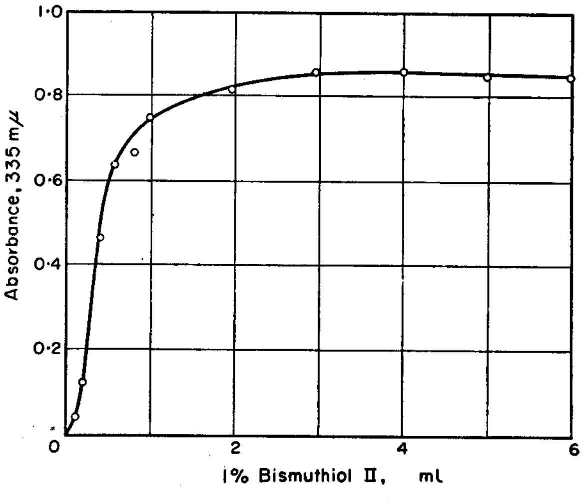

FIG. 3.—Effect of amount of bismuthiol II.

development of the tellurium colour. If EDTA is used to prevent the formation of insoluble hydroxides, it may be added after the tellurium colour has been developed at pH 2·2, and before the pH is adjusted to 6·5.

Effect of pH

The colour of the tellurium-bismuthiol II compound is developed only in acidic medium. If the solution is too acid, the bismuthiol II is precipitated in its acid form; if the pH of the solution is above 2·5, the formation of the tellurium-bismuthiol II compound is inhibited. It seems that the optimum pH for the colour development is at 2·0–2·3 (Fig. 4). Citric acid not only serves as a good buffer but also as a complexing

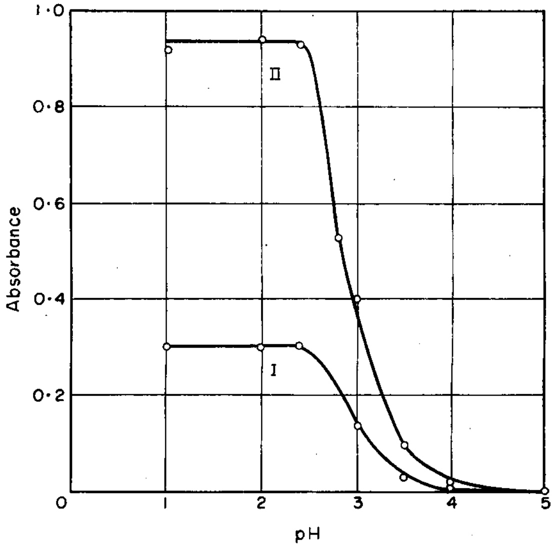

Fig. 4.—Effect of pH on colour development. I, 305 mμ: II, 340 mμ.

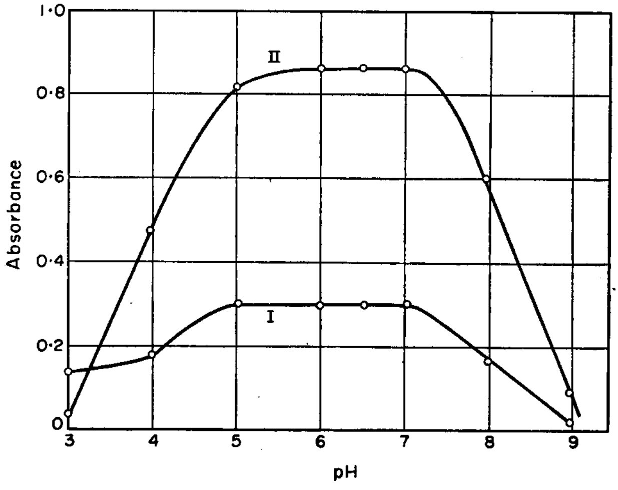

Fig. 5.—Effect of pH on solvent extraction. I, 395 mμ: II, 335 mμ.

agent to prevent hydrolysis of many metals. The amount of citric acid present has no effect. Tartaric acid may be used instead of citric acid. Fig. 5 shows that the coloured product is stable in neutral or slightly acid medium and that it decomposes in alkaline medium. For solvent extraction, the pH should be adjusted to 5–7. An optimum pH of 6·5 is chosen, because at this pH the amount of free bismuthiol II extracted is a minimum, and EDTA can mask the metals more effectively than in a more acidic medium.

Time required for colour development

The curve in Fig. 6 shows that the formation of the extractable reaction product required at least 20 min in order to obtain constant absorbance. It is believed that the reaction of tellurium with bismuthiol II is a slow process which is similar to that of selenium with diaminobenzidine at pH 2–3. In the reaction of tellurium and bismuthiol II, some unextractable intermediate products may be formed in less than 20 min.

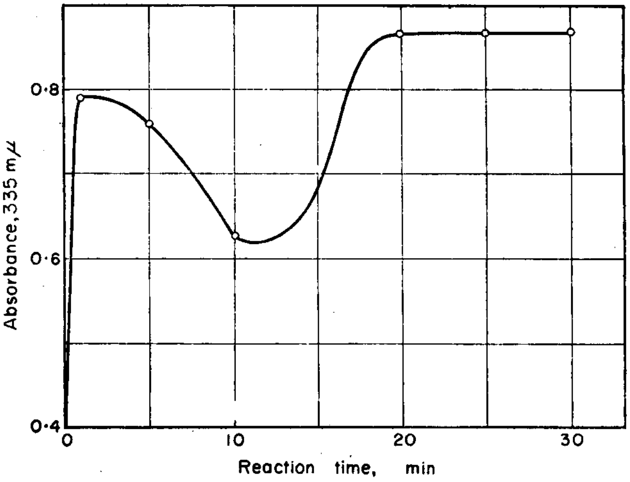

FIG. 6.—Effect of time on reaction.

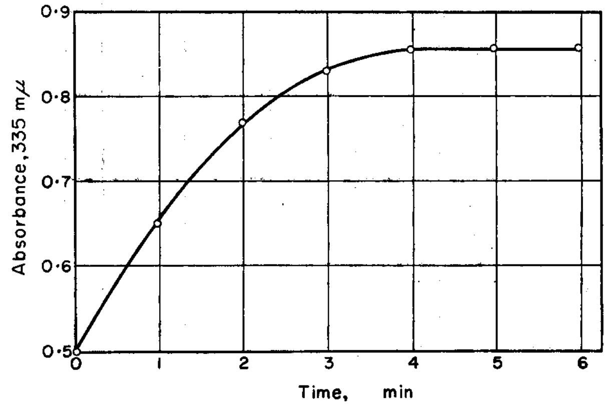

FIG. 7.—Effect of time on solvent extraction, no $(NH_4)_2SO_4$.

Effect of time of shaking

Fig. 7 shows that a minimum of 4 min of extraction time was required to obtain maximum extraction in the absence of sulphate. It was later found that the rate of extraction can be increased by addition of large amounts of sulphate. Extraction for 1 min with 3 g of ammonium sulphate gave slightly better extraction than extraction for 5 min without ammonium sulphate. Neither ammonium nitrate nor magnesium sulphate was as effective as ammonium sulphate in acting as a salting-out agent.

Beer's law and sensitivity

As indicated in Fig. 8, Beer's law is followed for both calibration curves in the range 5–50 μg of tellurium in 10 ml. It was also found that from 5–100 μg of tellurium in 10 ml of aqueous solution also followed Beer's law. The absorptivity was found to be 28,000 at 335 mμ and 14,700 at 395 mμ. The sensitivity was found to be 0.0005 μg of tellurium per cm^2 at 335 mμ and 0·009 μg of tellurium per cm^2 at 395 mμ.

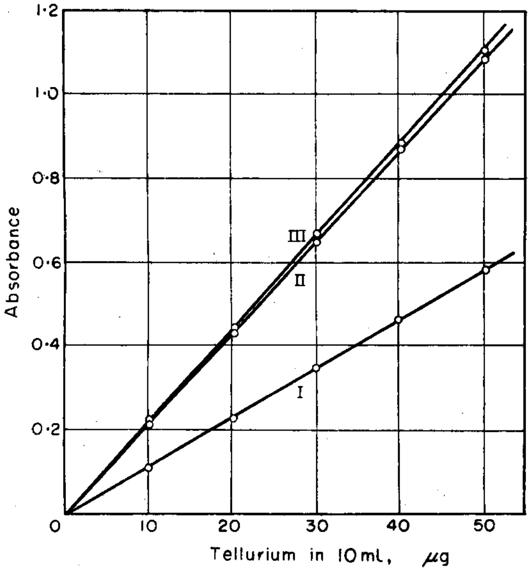

FIG. 8.—Calibration curves.
I—aqueous solution 395 mμ.
II—chloroform extract, 335 mμ, 5 min, no $(NH_4)_2SO_4$.
III—chloroform extract, 335 mμ, 1 min, 3 g $(NH_4)_2SO_4$.

Stability

The coloured product in chloroform was found to be stable for at least 24 hr. For the aqueous solution procedure, polyvinyl alcohol was used for preventing the formation of a precipitate. No appreciable turbidity was found after 1 hr. Turbidity may occur, however, after several hours.

Solvent extraction

Of the common solvents tried, chloroform and carbon tetrachloride were most satisfactory for extracting the coloured product of the reaction between tellurium and bismuthiol II (Table II). Isoamyl alcohol or hexanol extracted the yellowish compound, but the extract was turbid, and it was difficult to remove the white colloidal particles in the extract by filtration or centrifugation. The chloroform extract was clear. It was probable that the alcohol reacted with bismuthiol II to liberate colloidal sulphur.

TABLE II.—DIFFERENT SOLVENTS

20 μg Te in 10 ml

	Absorbance, 335 mμ	Remark
Chloroform	0·430	Clear
Carbon Tetrachloride	0·430	Clear
Isoamyl Alcohol	0·005	Turbid
n-Hexanol	0·005	Turbid
4-Methyl-2-pentanone	0·050	Yellow and turbid, including the reagent blank.

Addition of large amounts of salt such as ammonium chloride or potassium sulphate helped the extraction by isoamyl alcohol, n-hexanol, and 4-methyl-2-pentanone.

From Fig. 5 it can be concluded that the extraction must be carried out at pH 5–7. A similar explanation to that in the case of the extraction of piazselenol may be proposed. The reaction between tellurium and bismuthiol II in acidic medium may be written as indicated in Fig. 9.

The dissociation constant, k, for equation (1) is 6×10^{-9}.[7] The concentration of Te^{4+} ion is small at pH 2, but the tellurium bismuthiol II compound is a very stable one. In the presence of bismuthiol II the reaction in equation (1) moves from left to right. It would be expected in such a case that complete reaction needs a large excess of bismuthiol II and a long time for development. As shown in equation (2), the charged complex of tellurium and bismuthiol II is formed in acidic medium and its extractability depends upon the number of charges. The uncharged complex shown in equation (3), formed at pH > 5, is easily extracted by chloroform. At pH > 3, the acidity is not strong enough for the reaction in equation (1) to proceed from left to right, and therefore no Te^{4+} ion is available for formation of the complex of tellurium bismuthiol II. This explains that at first a pH of approximately 2 is required to ensure the reaction of free tellurium ion with bismuthiol II; once the tellurium bismuthiol II complex has been formed, it can be extracted by adjusting to pH 6–7 in order to neutralise the positive charges of the complex. In alkaline medium, the tellurium bismuthiol II complex may gradually decompose in favour of the formation of tellurite.

Selectivity

Bismuthiol II reacts with many metals. Some of them may be masked by EDTA and citrate, which also prevents the hydrolysis of heavy metals. The interferences of iron^{III} and copper are serious and cannot be masked by EDTA. Besides, strong oxidising agents react with bismuthiol II in a manner similar to tellurium. Large amounts of arsenic^{III} give a white precipitate with the reagent and interfere at 335 mμ. Since many methods are available for separating tellurium from other elements,

$$H_2TeO_3+4H^+{=}Te^{4+}+3H_2O \qquad (1)$$

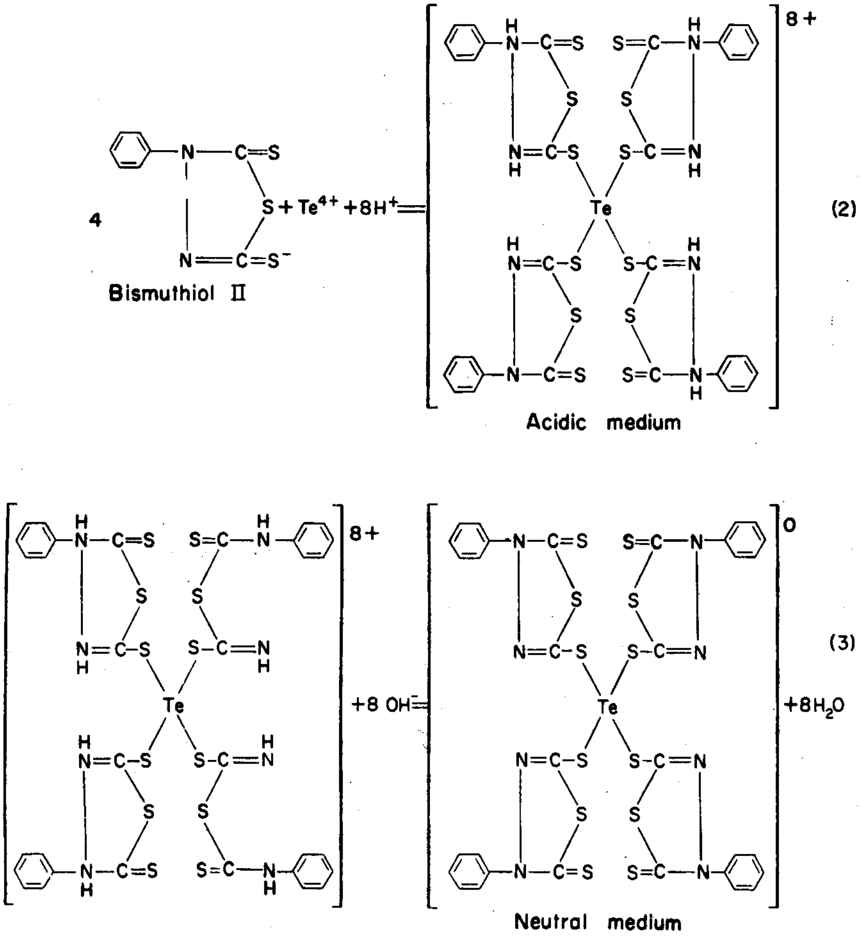

FIG. 9.

especially from selenium, it is better to separate tellurium from the others by co-precipitation with selenium in the elemental form. Selenium may be separated by bromine-hydrobromic acid evaporation or by diaminobenzidine. Many separation methods have been reviewed by Johnson.[2]

Interference studies

The metals interfering with this method have been described previously. Traces of iron and copper interfere. EDTA could not completely eliminate their interferences, since they still react with bismuthiol II at pH 2·2 in the presence of EDTA. Although they do not react with this reagent at pH > 6, the bismuthiol II complexes of iron and copper are not easily decomposed by EDTA at pH 6. Cyanide failed to mask copper at pH 2·2 but is effective at pH 6·5. Large amounts of arsenic^{III} give a white precipitate with the reagent at pH 2·2, and interfere at 335 mμ. Selenium reacts similarly to tellurium and must be removed before determination. Reaction of bismuth or cadmium with the reagent was not completely masked by EDTA at pH 2·2 but their bismuthiol II complexes were easily decomposed by EDTA at pH 6·5. Therefore small amounts of bismuth or cadmium can be tolerated. The results of determining tellurium in the presence of foreign ions are shown in Table III. In general, it is recommended that tellurium be separated from other interfering elements before employing bismuthiol II. Ferric hydroxide and aluminium hydroxide have been used as collecting agents for separating tellurium in its elemental form. Since beryllium does not react with bismuthiol II and EDTA, it would be advantageous to use beryllium hydroxide as a collecting agent in the presence of EDTA. If selenium is also present, both selenium and tellurium are separated along with beryllium hydroxide. The precipitates are then treated with bromine and hydrobromic acid to remove selenium. The bismuthiol II method is then followed. An attempt was made to separate tellurium from iron by a Dowex 50 cation-exchanger (hydrogen form); it was found that both iron and tellurium were absorbed by the resin. Chloride, bromide, sulphate, nitrate, and phosphate do not interfere.

TABLE III.—DETERMINATION OF TELLURIUM IN PRESENCE OF FOREIGN IONS
TELLURIUM TAKEN: 20·0 μg

Foreign ion	Amount added	Tellurium found, μg
Be^{2+}	0·05 m mole	20·0
Nb^{5+}	0·001 m mole	20·2
Al^{3+}	0·01 m mole	19·5
In^{3+}	1 mg	20·0
Ga^{3+}	0·1 mg	20·1
Bi^{3+}	0·1 mg	20·2
Fe^{3+}	13 μg	24·0
Cu^{2+}	10 μg	20·7
As^{3+}	47 μg	20·4
Cd^{2+}	1 mg	20·0

Determination of tellurium in selenium

It would be interesting to determine traces of tellurium in selenium because not only selenium in general interferes with the methods for tellurium but also it is a good co-precipitating agent for separating traces of tellurium. For employing the proposed method, selenium must be removed before determination of tellurium. Bromine and hydrobromic acid have been used for removing selenium.[11] A study was made to test the feasibility of the bromine-hydrobromic acid method to remove large amounts of selenium in the determination of traces of tellurium.

Synthetic mixtures containing 1–2 mg of selenium and 0–40 μg of tellurium were prepared. To the mixture (5 ml) in a 100-ml beaker was added 0·5 ml of redistilled hydrobromic acid. Some bromine vapour was introduced. The mixture was evaporated on a hot plate at 100° or in a water bath. After drying, the operation was repeated three times by the addition of 1 ml of hydrobromic acid (rinsing down the side of the beaker) and the introduction of bromine vapour. Finally, the residue was baked at 100° for 10 min in order to expel any traces of bromine and hydrobromic acid, which also react with bismuthiol II. The beaker was cooled, 1 ml of 1M citric acid, 6 ml of ammonium sulphate solution, 20 ml of water, and 3 ml of 1% bismuthiol II solution were added. The solution was set aside for 20–30 min, and then extracted with 10 ml of chloroform, after adjusting the pH to 6·5. The results shown in Table III are excellent.

If high sensitivity is not required, after removing selenium the tellurium may simply be determined in aqueous solution instead of using solvent extraction. The excellent recovery of traces of tellurium suggests that selenium can be used to collect traces of this element and thus separate it from others. No loss of tellurium was noticed during volatilisation of selenium with bromine–hydrobromic acid.

TABLE IV.—DETERMINATION OF TELLURIUM IN MIXTURES OF SELENIUM-TELLURIUM AFTER VOLATILISATION OF SELENIUM AS BROMIDE

Tellurium present, µg	Tellurium found, µg	
	1 mg Se added*	2 mg Se added†
none	0	0
20·0	20·0	20·0
30·0	29·8	29·5
40·0	40·0	39·8

* Chloroform extraction procedure.
† Aqueous solution procedure.
For 30·0 µg of tellurium without addition of selenium, recovery of 30·0 µg of tellurium was obtained in both aqueous and chloroform procedures.

Composition of compound

The Job's curves shown in Fig. 10 obtained in aqueous solution at 395 mµ indicate that a complex of 1 tellurium:4 bismuthiol II was formed. It was thought that the reaction between tellurium and bismuthiol II might be a redox reaction. In order to confirm the presence of tellurium, the precipitate was dissolved in a dilute potassium hydroxide solution using heat. The solution was adjusted to pH 8 with hydrochloric acid and sodium carbonate. Small amounts of EDTA and cyanide were added, followed by 1 ml of 1% sodium diethyldithiocarbamate solution. The chloroform

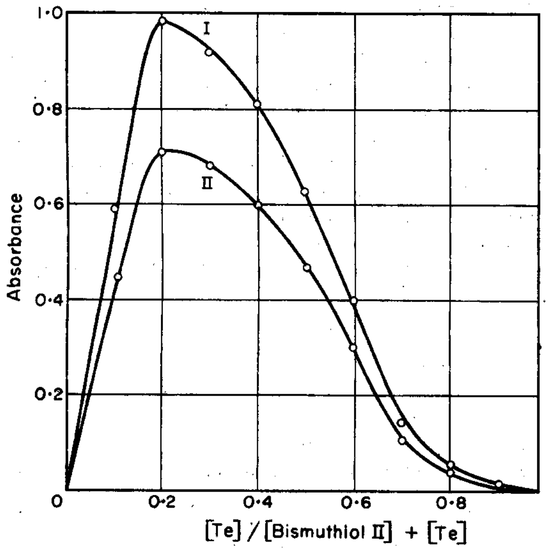

FIG. 10.—Job's curves (total concentration = $3{\cdot}2 \times 10^{-4}$ M. I, 400 mµ: II, 420 mµ.)

extract was decomposed with a mixture of nitric acid and perchloric acid and then tested with diethyldithiocarbamate in the presence of EDTA and cyanide. Tellurium was found in both the precipitate and the chloroform extract. It is known that the palladium bismuthiol II complex has a 1 : 2 composition[10] and the bismuth bismuthiol II complex has a 1 : 3 composition.[12] The tellurium bismuthiol II complex would be expected to have a composition of 1 : 4. Based on the presence of tellurium in the reaction product, the Job's curves, and the fact that tellurium has less tendency to be co-ordinated, the tellurium bismuthiol II complex may be presumed to be a salt, with the structure shown above. The Job's curves also show that complexes with other compositions may also be formed when tellurium is in excess.

Zusammenfassung—Ein spectrophotometrische Studie der Reaktion zwischen Tellur und Bismuthiol II wurde angestellt um die Brauchbarkeit der Reaktion zur Bestimmung von Tellur sicherzustellen. Der Reaktionsmachanismus wird diskutiert. Die gelbe Verbindung entsteht bei pH 2–2·2, ist stabil und wird durch Chloroform bei pH kleiner als 5 quantitativ extrahiert. Zwei Methoden werden vorgeschlagen. Eine arbeitet mit wässriger Lösung bei einem Absorptionsmaximum bei 395 mμ, die zweite nach Solventextraktion bei 335 mμ. Die zweite Methode ist selektiver und empfindlicher. Zahlreiche der gewöhnlichen Metallionen stören nicht, wenn ÄDTE und Zitrat als Maskierungsmittel anwesend sind. Störungen durch Quecksilber, Eisen, Kupfer und Selen sind schwer. Beryllium und Selen können als Sammler verwendet werden um Tellur abzutrennen, wenn ÄDTE gegenwärtig ist. Selen ist anschliessend durch Behandlung mit Brom und Bromwasserstoffsäure zu verflüchtigen. Der Absorptionskoeffizient ist 28,000 bei 335 mμ und die Empfindlichkeit bei derselben Wellenlänge ist 0.005 μg Tellur per cm².

Résumé—Les auteurs ont fait une étude spectrophotométrique de la nouvelle réaction tellure-bismuthiol II pour le dosage de traces de tellure. Le mécanisme de la réaction est disucté. Le composé jaune du tellure formé à pH 2,0–2,2 est stable et extrait quantitativement par le chloroforme à un pH supérieur à 5. L'addition de sulfate d'ammonium augmente la vitesse de l'extraction. Deux modes opératoires sont proposés: en solution aqueuse avec un maximum d'absorption à 395 mμ ou extraction par un solvant avec un maximum d'absorption à 335 mμ. La technique par extraction rend la méthode plus sélective et plus sensible. De nombreux ions courants ne gênent pas quand on utilise l'EDTA et le citrate comme agents complexants. Le mercure, le fer, le cuivre et le sélénium gênent sérieusement. Le béryllium ou le sélénium peuvent être utilisés comme agent collecteur en présence d'EDTA pour la séparation du tellure. Le sélénium peut être séparé par volatilisation avec du brome et de l'acide bromhydrique. Les valeurs respectives suivantes ont été trouvées pour l'absorption et la sensibilité de la réaction: 28.000 et 0,005 μg de tellure par cm² à 335 mμ.

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EINE NEUE POLARIMETRISCHE METHODE ZUR BESTIMMUNG VON OPTISCH INAKTIVEN IONEN—I

BESTIMMUNG DES QUECKSILBERS

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Zusammenfassung—Es wird eine neue allgemein anwendbare Methode zur polarimetrischen Bestimmung von optisch inaktiven substanzen beschrieben. Zu diesem Zweck wird das betreffende Ion (im Falle einiger Kationen nach vorherigem Anionisieren) mit Hilfe eines optisch aktiven Reagenz gefällt oder in eine Komplexverbindung übergeführt. Das Reaktionsprodukt wird isoliert, gelöst und polarimetriert. Als Beispiel wird die Bestimmung des Quecksilbers erläutert. Das Hg^{2+}-Ion wird mit Hilfe von Kaliumjodid in Tetrajodomerkuriat übergeführt und dann mit einer Chininmonochlorhydratlösung gefällt. Der filtrierte und gut gewaschene Niederschlag wird in Aceton gelöst und die so erhaltene Lösung bei Zimmertemperatur polarimetriert.

IM folgenden wird eine neue polarimetrische Methode zur Bestimmung optisch inaktiver Ionen beschrieben.

Dieser Methode können folgende allgemeine Reaktionen zugrunde liegen:

$$A + R_a = C_a \qquad (1)$$

$$A + R_i = C_i \qquad (2)$$

$$C_i + R_a' = D_a \qquad (2')$$

A = ein zu analysierender Stoff; R_a = ein optisch aktives Reagens (Kation, Anion oder ein Komplex-bzw. Chelatbildner); C_a = eine leicht oder schwerlösliche optisch aktive Verbindung: Salz oder Komplex; R_i = ein optisch inaktives einfaches Anion oder eines, das Chelate zu bilden fähig ist; C_i = ein optisch inaktives Anion oder Kation; R_a' = ein optisch aktives Kation oder Anion; D_a = eine schwerlösliche, optisch aktive Verbindung.

Falls ein Niederschlag entsteht (D_a u. C_a), wird dieser abfiltriert, vom R_a- oder R_a'-Überschuss durch Waschen befreit, gelöst, in einen Messkolben gebracht und polarimetriert. Der Niederschlag kann auch durch Extraktion abgetrennt werden, selbstverständlich unter der Voraussetzung, dass nicht auch ein Teil des optisch aktiven Reagensüberschusses (R_a bzw. R_a') extrahiert wird.

Falls eine lösliche optisch aktive Verbindung entsteht (Gleichung 1), wird diese durch Extraktion getrennt, in einen Messkolben gebracht und polarimetriert.

Das Lösungsmittel wird so gewählt, dass es keinerlei Einfluss auf das Drehungsvermögen der optisch aktiven Verbindung haben kann.

Die Methode ist allgemein anwendbar, ist leicht auszuführen und weist gegenüber der kolorimetrischen den Vorteil einer linearen Abhängigkeit des Drehungsvermögens von der Konzentration—wie sie ein Gesetz vom Typ Bouguer-Lambert-Beer fordert—in viel weiteren Grenzen auf.

Vor allem ist die Bestimmung von Anionen nach vorhergehender Fällung mit organischen optisch aktiven Basen sehr bequem.

Die Kationen werden zuerst in negative Säurekomplexe übergeführt und dann mit optisch aktiven organischen Basen gefällt.

Als Fällungskationen kann eine optisch aktive organische Base bzw. ihr Salz (Chinin, Codein, Morphin, Cinchonidin, Cinchonin, Conchinin, Nicotin, Thebain, Strychnin, ua.), oder ein optisch aktives Oniumsalz (Tetralkylammonium, Phosphonium, Arsonium, Sulfonium, usw.) benützt werden.

Anhand dieser Methode können nachstehende Ionen bestimmt werden: Heteropolysäuren; Bi^{3+}, Cd^{2+}, Hg^{2+} nach vorangehender Überführung in Iodokomplexe; Fe^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+} nach Überführung in Cyanokomplexe; Hg^{2+} in Form von $HgCl_2$ oder nach Überführung in Thiocyanatokomplexe; Au^{3+}, Pt^{4+} nach Überführung in Chlorokomplexe; UO_2^{2+} als Salicylatkomplex; MoO_4^{2-}, WO_4^{2-}, I^-, Br^-, CN^-, SCN^-, usw.

Die Genauigkeit und Empfindlichkeit der Methode kann auf nachstehende Weise erhöht werden:

(1) Fällung mit Stoffen von grossem molekularen Drehungsvermögen.

(2) Polarimetrieren im Spektralgebiet grösster molekularer Drehung des aktiven Stoffes. Es ist zweckmässig die Rotationsdispersion jedes zur Fällung benutzten Stoffes zu kennen.

(3) Benutzung eines objektiven Apparats, z.B. eines photoelektrischen Spektralpolarimeters.

(4) Heranziehen des Faraday' schen Effektes durch Kompensation der Drehung mit Hilfe eines magnetischen Feldes und Bestimmung der erforderlichen Stromstärke.

Zur Illustration dieser Arbeitsweise sei die Bestimmung des Quecksilbers beschrieben.

Die Methode beruht auf den Reaktionen (2) u. (2′) und zwar führt man das Hg^{2+}-Ion zuerst mit Hilfe von Kaliumjodid in den Komplex $[Hg_4]^{2-}$ über, der dann mit einem organischen optisch aktiven Kation (Chinin) bei Zimmertemperatur gefällt wird. Nach Abfiltrieren des Niederschlages und entfernen des Chininchlorhydrats durch gründliches Waschen, wird er in Aceton gelöst. Man polarimetriert dann die acetonische Lösung des Chinintetraiodomerkuriates.

ARBEITWEISE

Die 10–300 mg Hg enthaltende Lösung (höchstens 100 ml) des Merkurisalzes wird mit einer 2% igen wässerigen KJ-Lösung tropfenweise bis zum Lösen des HgJ_2-Niederschlages, versetzt. Das gebildete $[HgJ_4]^{2-}$ -Anion wird dann mit einer 5%-igen Chininmonochlorhydratlösung im Überschuss bei Zimmertemperatur gefällt. Es bildet sich Chinintetrajodomerkuriat $(C_{20}H_{25}O_2N_2)$ $[HgJ_4]$. ein weisser (in Säuren schwer löslicher) Niederschlag, den man abfiltriert und mit kaltem Wasser 5–6 mal wäscht.

Der vom Chininüberschuss befreite Niederschlag wird auf dem Filter in Aceton gelöst und die so erhaltene Lösung in einem Messkolben (100 ml) aufgefangen. Man wäscht das Filter gut mit Aceton und füllt den Kolben mit Wasser bis zum Marke auf. Die acetonisch Lösung des Chinintetrajodomerkuriats wird bei Zimmertemperatur polarimetriert.

Wir fanden, dass weder eine Temperaturerhöhung von 20° bis 50°, noch das Verhältnis Aceton: Wasser noch das Ansäuren der Lösung mit HCl, einen Einfluss auf den Rotationswinkel haben.

Es wurde mit einem Lippich-Halbschattenpolarimeter mit Na-Lampe gearbeitet, das eine Genauigkeit von 36″ (1°/100) erlaubte, die Rohrlänge betrug 20 cm.

Eine Bestimmung dauert nicht länger als 30 min.
Die Messergebnisse sind in Tabelle I und Figur 1 wiedergegeben.

TABELLE I

$\alpha_0 = 2°51'36''$

mg Hg/100 ml, y	α	$\alpha - \alpha_0$	$\alpha - \alpha_0$ im 1°/100, x
9·98	2°45′	6′36″	11
19·90	2°41′24″	10′12″	17
39·94	2°31′48″	19′48″	33
59·90	2°22′12″	29′24″	48
79·87	2°15′	36′36″	61
99·84	2° 6′36″	45′	75
139·77	1°48′	1° 3′36″	106
159·74	1°43′48″	1° 7′48″	113
179·71	1°34′12″	1°17′24″	129
199·68	1°22′12″	1°29′24″	149
299·52	0°45′	2° 6′36″	211

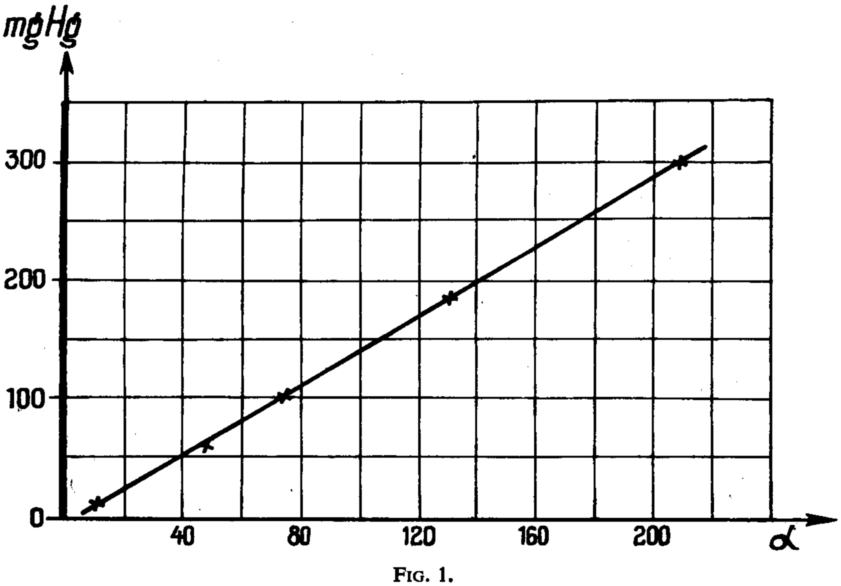

FIG. 1.

Nach Verarbeitung der Ergebnisse der 11 Bestimmungspaare mit Hilfe der Methode der kleinsten Quadrate, wurden die Koeffizienten A_0 und A_1 der Gleichung $y = A_0 + A_1x$, die zur Berechung der Quecksilbermenge (in mg) dient, aus dem Rotationswinkel x (in 1/100° ausgedrückt) berechnet. Man erhält die für die obigen Arbeitsbedingungen gültige Funktion $y = -7{,}1 + 1{,}433x$ = mg Hg/100 ml.

Summary—A new general method for the determination of optically inactive substances is described. The ion to be determined, as such, or after anionisation (in the case of cations), is precipitated, or is converted into a complex by means of an optically active reagent. The reaction product is dissolved and the rotation is determined. For example, the ion Hg^{2+} is converted by means of potassium iodide into the tetra-iodomercurate, which is precipitated with a solution of quinine hydrochloride. The precipitate is filtered off, washed and dissolved in acetone; the rotation of the resulting solution is determined at room temperature.

Résumé—Une nouvelle méthode générale de dosage de substances optiquement inactives est basée sur la précipitation des anions (ou des cations après transformation en anions) par un agent complexant optiquement actif. Le produit de la réaction est dissous et le pouvoir rotatoire est déterminé. Les auteurs décrivent le dosage du mercure. L'ion mercurique est transformé au moyen d'iodure de potassium en anion tétra-iodo mercurate, qui est précipité par du chlorhydrate de quinine. Le précipité est filtré, lavé et dissous dans l'acétone, et le pouvoir rotatoire est déterminé à la température ambiante.

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SEPARATION AND DETERMINATION OF SCANDIUM USING *N*-BENZOYLPHENYLHYDROXYLAMINE*

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Summary—Scandium may be determined using *N*-benzoylphenylhydroxylamine, which precipitates a complex containing scandium and reagent in the ratio 1:3. This precipitate may be utilised for the gravimetric determination of scandium by conversion to Sc_2O_3 at 600°. It is possible to separate scandium from zirconium, titanium and the rare earth elements by extraction.

THE analytical reactions of scandium have not been studied to any great extent.[1] For its separation from other elements and quantitative determination several inorganic precipitants have been recommended, *e.g.* hydrofluoric, fluorosilicic, pyrophosphoric, hypophosphorous acids, *etc.* Organic precipitants for scandium have been less studied. For the separation of scandium from other elements, ion-exchange chromatography and extraction with organic solvents have been used.

In the present work to select new reagents for scandium, the similarities with the quadrivalent elements zirconium, hafnium and thorium, brought about by the close values of the ionic radii of these elements, have been taken into account. As an analogue for cupferron, *N*-benzoylphenylhydroxylamine was used. This is a reagent for the determination of titanium, vanadium, molybdenum, niobium, tantalum and other elements. Our experiments showed that in a strongly acid medium *N*-benzoylphenylhydroxylamine precipitates zirconium quantitatively and, in a weakly acid medium, thorium and scandium. The conditions for the precipitation and extraction of the *N*-benzoylphenylhydroxylaminate of scandium and the composition of the precipitate were determined. Examples of the separation of scandium from zirconium and the rare earth metals are given here.

The *N*-benzoylphenylhydroxylamine reagent was synthesised by Shome's method[2] and the scandium chloride solution was prepared by dissolving spectrally pure scandium oxide in the minimum quantity of concentrated hydrochloric acid with continuous careful heating until the cloudiness disappeared. The solution obtained was evaporated almost to dryness, and the residue was dissolved in the necessary volume of water. The titre of the solution was determined by precipitation of the hydroxide with ammonia and weighing as Sc_2O_3. For complete precipitation of the scandium it is necessary to add a small excess of reagent and keep the pH $>5{\cdot}2$. The results of quantitative determinations of a pure scandium salt solution are shown in Table I.

To study the composition of the scandium *N*-benzoylphenylhydroxylaminate the precipitate was filtered off in a sintered-glass filter-crucible, washed with 50 ml of hot water and 30–50 ml of ether, then dried to constant weight at 105°–110°. Part of the precipitate was then heated to constant weight at 800°–900°. The results showed

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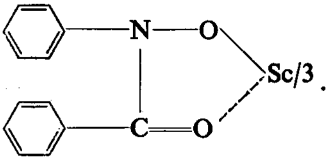
* Translated from the Russian, *Zavodskaya Lab.*, 1959, **12**, 1435.

TABLE I.—DETERMINATION OF SCANDIUM WITH N-BENZOYLPHENYLHYDROXYLAMINE

Sc_2O_3, *mg*	
Taken	Found
4·5	4·5; 4·6; 4·5; 4·5
2·7	2·7; 2·8; 2·7
3·6	3·7
1·8	1·8

that the chemical composition of the precipitate separating from a weakly acid solution corresponds with the formula



To find the stability of scandium N-benzoylphenylhydroxylaminate to heat we carried out a thermogravimetric analysis (Fig. 1). The precipitate was stable up to 220°.

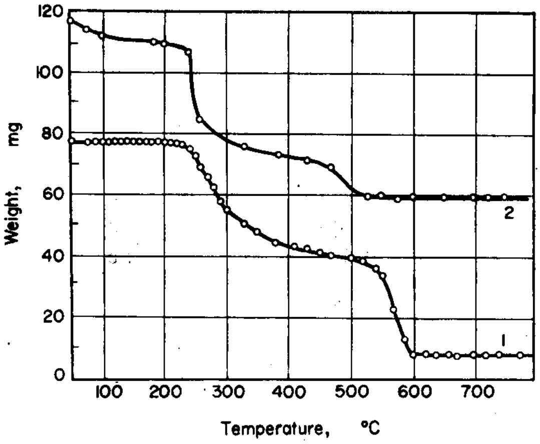


FIG. 1.—Results of thermogravimetric analysis.
1.—*N*-Benzoylphenylhydroxylaminate of scandium.
2.—Cupferrate of scandium.[4]

To obtain the form used for weighing (Sc_2O_3), the precipitate need only be heated to 600°.

Scandium may be separated from the rare earth elements as follows. To 100 ml of a solution containing scandium and rare earth elements 30 ml of a 20% solution of ammonium acetate were added and a few ml of acetic acid (1 : 1), so that after precipitation the solution pH should be about 5·4. After precipitation of the scandium, ammonium was added to the filtrate and the precipitate of rare earth hydroxide was filtered off through a fine filter, dried and heated to constant weight at 800°–900°. The results are shown in Table II.

TABLE II.—SEPARATION OF SCANDIUM FROM RARE EARTH ELEMENTS

Taken, *mg*		Found, *mg*	
Sc_2O_3	Σ Rare earths	Sc_2O_3	Σ Rare earths
4·5	4·9	4·6 and 4·5	4·9
4·5	29·7	4·6 and 4·7	29·6 and 29·5
2·7	29·7	2·6	29·7
1·8	79·2	1·8	79·3

Zirconium in a strongly acid medium (3*N* hydrochloric acid) is precipitated quantitatively by *N*-benzoylphenylhydroxylamine, while scandium is not precipitated under these conditions. The separation of scandium and zirconium can be carried out using this fact. For this purpose a titrated solution of zirconium oxychloride was used. Firstly the zirconium was precipitated in a 2*N* hydrochloric acid solution. The filtrate was evaporated to about 100 ml and the excess hydrochloric acid was neutralised with ammonia, using methyl orange as indicator. The precipitation and determination of the scandium was carried out subsequently (Table III).

Scandium *N*-benzoylphenylhydroxylaminate can be extracted with n-butyl alcohol, amyl acetate, benzene, chloroform and iso-amyl alcohol. To determine the conditions for extraction, a measured amount of scandium chloride solution from a pipette was introduced into a 30-ml separating funnel. This was diluted with distilled water to a given volume, then dilute hydrochloric acid or ammonia was added to give the required pH. An equal volume of reagent was then added, in iso-amyl alcohol. After shaking, the scandium which had passed into the organic solvent and that remaining in the aqueous phase were determined spectrophotometrically using the reaction with Alizarin Red-S. The effect of the organic substances was taken into account using the method of Eberle and Lerner.[3]

TABLE III.—SEPARATION OF SCANDIUM FROM ZIRCONIUM

Taken, mg		Found, mg	
Sc_2O_3	ZrO_2	Sc_2O_3	ZrO_2
2·7	3·2	2·6 and 2·7	3·3 and 3·2
4·5	16·0	4·6	16·0
3·6	16·0	3·6	16·0
1·8	48·0	2·0	47·8
2·7	48·0	2·9	47·9

To determine the amount of scandium extracted by the organic solvent two extractions were carried out, with shaking, using 5 ml of 1–2*N* hydrochloric acid. The aqueous phase containing the scandium was introduced into a 100-ml volumetric flask. To this solution a few ml of distilled water were added and 2 ml of a 0·1% alizarin red-S solution, and the liquid was carefully neutralised with ammonia (1:3) until a red colour appeared. Then 5 ml of a 20% buffer solution of ammonium acetate (pH 3·5) were added, the solution was cooled to room temperature, and was diluted with water to an exact volume. The absorption was measured spectrophotometrically at 520 mμ in a 5-cm cell. The results obtained are shown in Figs. 2 and 3.

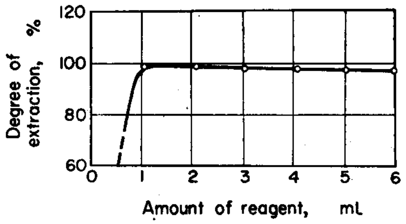


FIG. 2.—Extraction of the *N*-benzoylphenylhydroxylaminate of scandium with various amounts of reagent (0·5% solution of N-benzoylphenylhydroxylamine in iso-amyl alcohol).

The distribution equilibrium occurred quickly. Shaking for 4 min produced quantitative separation of the scandium. The presence of NH_4^+, Na^+, NO_3^- and Cl^- ions produced no noticeable effect on the degree of extraction.

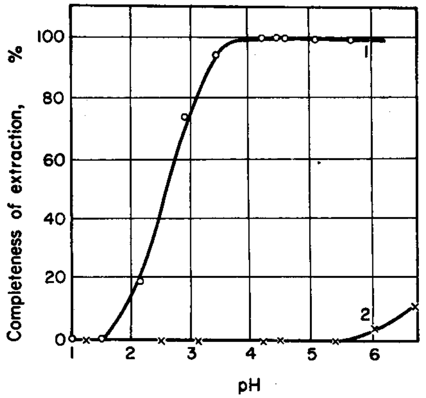


FIG. 3.—Extraction of the *N*-benzoylphenylhydroxylaminates of scandium and rare earth elements at various pH of the aqueous phase:
1.—Scandium extractions.
2.—Σ Rare earth elements extraction.

A study of the extraction of the rare earth elements showed that at pH $<5{\cdot}8$ *they are not extracted (see Fig. 3, curve 2). This fact was used for separating them from the scandium at pH* $\sim 4{\cdot}5$. *Our experiments also showed that the N-benzoyl-*

TABLE IV.—SEPARATION OF SCANDIUM FROM RARE EARTH ELEMENTS, ZIRCONIUM AND TITANIUM BY EXTRACTION

Taken, *mg*			Found, *mg*
Sc_2O_3	Oxides of other metals		
0·025	rare earth	10	0·027
0·025	rare earth	30	0·027
0·050	rare earth	10	0·050
0·050	rare earth	30	0·051
0·075	rare earth	10	0·074
0·075	rare earth	30	0·077
0·025	ZrO_2	4·8	0·026
0·050	ZrO_2	3·2	0·052
0·075	ZrO_2	3·2	0·075
0·025	TiO_2	1	0·026
0·050	TiO_2	1	0·053

phenylhydroxylaminates of zirconium and titanium are extracted quantitatively in a strongly acid medium, with iso-amyl alcohol (for zirconium 1–8*N* hydrochloric acid; for titanium 5–10*N* hydrochloric acid), while the scandium is not extracted. A method for the separation of scandium from zirconium and titanium can be based on this fact. To carry out this separation zirconium in 2*N* hydrochloric acid and titanium in 5*N* hydrochloric acid were extracted twice (5 ml) with a 3% solution of *N*-benzoylphenylhydroxylamine in iso-amyl alcohol. The results are shown in Table IV.

Zusammenfassung—Scandium kann mit n-Benzoylphenylhydroxylamin als ein Komplex gefällt werden, der Metall und Reagens im Verhältnis 1:3 enthält. Scandium wird gravimetrisch bestimmt; nach Verglühen zum Sesquioxyd bei 600°C. Die Trennung des Scandiums von Zirkon, Titan und seltenen Erden mittels Extraktionsmethoden ist möglich.

Résumé—Le scandium peut être précipité par la n-benzoylphénylhydroxylamine sous forme d'un complexe contenant scandium et réactif dans le rapport 1/3. Ce précipité peut être utilisé pour le dosage gravimétrique du scandium par transformation en SC_2O_3 à 600°. Il est possible de séparer e scandium du zirconium, du titane et des terres rares par extraction.

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ACTIVATION ANALYSIS OF MANGANESE IN CAST IRON AND HIGH-ALLOY STEELS

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Summary—A method for the determination of manganese in cast iron and high-alloy steels has been developed. Self-shielding errors and neutron flux irregularities were avoided by the use of an internal standard. Two procedures, integral counting and pulse height discrimination were used. The method was tested on standard samples. The results obtained on samples with a widely differing composition are in excellent agreement with those obtained by classical chemical analysis.

INTRODUCTION

ACTIVATION analysis with thermal neutrons is not only capable of high sensitivity for a large number of elements, but also allows accurate determinations as a non-destructive method of analysis. This was clearly demonstrated by several authors, among them Leliaert *et al.*,[1–3] who determined vanadium and tungsten in high alloy steels using an internal standard technique.[3]

In this paper an investigation of the direct determination of manganese in cast iron and high-alloy steels without chemical separation is described; iron or other long living species present in the high-alloy steels were used as internal standard.

As manganese has a quite large cross-section for thermal neutrons and a rather short half-life, high disintegration rates can be expected even after short irradiations at a moderate neutron flux.

Several authors have already determined manganese by activation analysis, namely Bowen[4] in biological material, Daudel[5] in aluminium alloys and Fisher *et al.*[6] in cobalt samples.

NUCLEAR DATA

Natural manganese occurs as the single isotope ^{55}Mn and gives rise to only one radioactive species, ^{56}Mn, a complex β-γ-emitter with 2·58 hr half-life, activation cross-section 13·4 barn. The decay scheme[7] is given in Fig. 1.

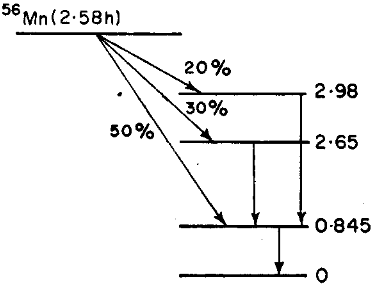

FIG. 1.—Decay scheme of ^{56}Mn.

Interfering activities arising from steel constituents

It is obvious that by thermal-neutron-activation of cast iron or high-alloy steels a large number of radioactive species can be formed, as appears from Table I.

TABLE I.—RADIOACTIVE SPECIES PRODUCED FROM CAST-IRON OR STEEL CONSTITUENTS

Element	% in steel	Natural isotope	$\theta \cdot \sigma_{act}$	Isotope produced	$T_{1/2}$	Radiation and energy
V	<2·5	^{51}V	4·5	^{52}V	3·75 m	β^- 2·7//γ 1·46
Cu	0·1	^{65}Cu	0·68	^{66}Cu	5·1 m	β^- 2·63/1·59//γ 0·191
Ti	up to 50	^{50}Ti	0·007	^{51}Ti	5·8 m	β^- 1·5/2·13//γ 0·3/0·6/0·9
Nb	0·30	^{93}Nb	1·4	^{94m}Nb	6·6 m	β^- 1·3//γ 0·04/0·9
Co	up to 45	^{59}Co	17	^{60m}Co	10·5 m	γ 0·058
Mo	seldom 2	^{100}Mo	0·019	^{101}Mo	14·6 m	β^- 2·2/1·2//γ 0·96/0·191
Mn	0·25–1·3	^{55}Mn	13	^{56}Mn	2·56 h	β^- 2·86/1·05/0·75// γ 1·77/0·82/2·06
Ni	up to 40	^{64}Ni	0·03	^{65}Ni	2·59 h	β^- 2·09//γ 1·49/1·12
Cu	0·1	^{63}Cu	2·97	^{64}Cu	12·9 h	E.C./β^+/β^-//γ 1·34
Mo	seldom 2	^{98}Mo	0·03	^{99}Mo	68 h	β^- 1·23/0·45/0·2// γ 0·74/0·18/0·14/0·78/0·36
Cr	up to 20	^{50}Cr	0·73	^{51}Cr	27 d	E.C.//γ 0·32
Fe	chief const.	^{58}Fe	0·0026	^{59}Fe	45 d	β^- 0·26/0·46//γ 1·28/1·1
Ta	1·2	^{181}Ta	21	^{182}Ta	118 d	β^- 0·53/1·1//γ 0·05/1·2
Co	up to 45	^{59}Co	34	^{60}Co	5·2 y	β^- 0·309/1·48//γ 1·17/1·33

It is, however, possible to correct for these interferences by analysis of the composite decay curve.

After irradiation runs of approximately 10 min, integral γ-counting was started after 4 hr, so that short living species such as ^{52}V, ^{66}Cu, ^{51}Ti, ^{94m}Nb, ^{60m}Co, ^{101m}Mo have completely decayed.

The other radioactive species which can be expected in high-alloy steels have half-lives considerably larger than ^{56}Mn so that an analysis of the decay curve causes no serious problem. Exception should, however, be made for ^{65}Ni, with a half-life practically identical with that of ^{56}Mn. The excitation cross-section of ^{64}Ni is, however, quite small (0·03 barn) and in 56% of the disintegration mode no γ-rays are emitted. Experimental results showed that a Ni:Mn ratio of 10 will cause an interference of only 0·1%.

Interfering activities due to the steel constituents can, however, be completely avoided by making use of a pulse-height discriminator set to count only γ-rays with an energy higher than 1·5 MeV. This technique allows a specific counting of ^{56}Mn, as it is the only γ-emitter present in high-alloy steels having an energy higher than this pre-set level. This counting technique makes analysis of the decay curve unnecessary, and thus avoids concomitant errors.

Interference due to (n,p) and (n,α) reactions

Interference from the $^{56}Fe(n,p)^{56}Mn$ reaction, because of the fast neutron flux in the reactor core, can cause an appreciable error, since iron is the main constituent. Although the cross-section of this reaction was determined by Mellish *et al.*,[8] who reported a value of 0·44 millibarn, it seemed advisible to determine experimentally the reaction yield as a function of the cadmium ratio, the fast flux distribution in the BR-1 reactor not being known with sufficient accuracy. The cadmium ratio can be regarded as a measure of the fast to thermal flux ratio. Cadmium has a cut-off value for neutrons with energy lower than approximately 0·4 eV.

Samples of pure Fe_2O_3 (Johnson Matthey) were irradiated in the reactor core (positions 1 and 2) and in the reflector (positions 3 and 4). The activities due to ^{56}Mn and ^{59}Fe were computed by analysis of the decay curve using a well-type scintillation counter. The cadmium ratios were determined with gold foils (200 mg/cm^2) wrapped in cadmium foil (thickness 0·75 mm).

The results expressed as the ^{56}Mn:^{59}Fe count rate ratio at a time t_0 (end of irradiation) as a function of the Cd ratio are represented in Fig. 2.

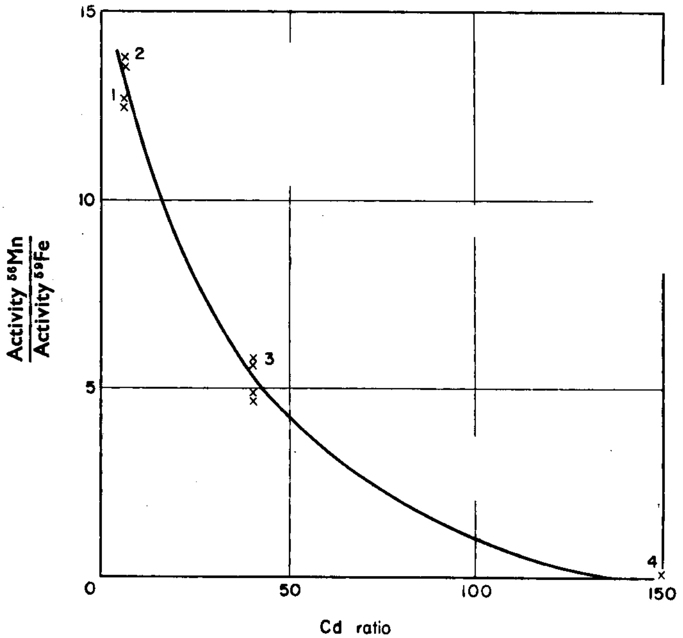

Fig. 2.—^{56}Fe(n,p)^{56}Mn reaction as a function of cadmium ratio.
1, 2—Reactor core
3, 4—Reflector.

Numerical values of thermal and fast neutron fluxes available at the different sites, and measured specific activities of the manganese, are summarised in Table II. The values given are integral counting rates extrapolated at a time t_0 for an irradiation of 1 hr.

Interference from the ^{59}Co(n,α)^{56}Mn reaction is also possible when irradiating in the reactor core, as cobalt can occur in large concentrations in high-alloy steels, although the cross-section according to Samsahl *et al.*[9] for the n,α reaction is only 0·14 millibarn.

To determine the extent of this interference, the same technique was used as described for iron, using Co_3O_4 (Johnson Matthey) as target material. After the decay of ^{60m}Co, the activity of the Co samples was followed during several hours but no activity due to ^{56}Mn could be found.

TABLE II

Site	F in n/cm^2/sec	Cd ratio	counts ^{56}Mn/ min/mg Fe	counts ^{59}Fe/ min/mg Fe	$\frac{\text{counts } ^{56}\text{Mn}}{\text{counts } ^{59}\text{Fe}}$
1	1·4 10^{12}	5·3	199	16	12·5
1	1·4 10^{12}	5·3	266	20·8	12·7
2	8·10^{11}	5·6	148·5	11	13·5
2	8·10^{11}	5·6	221	16·1	13·7
3	2·10^{11}	40	14	3·28	4·3
3	2·10^{11}	40	12·6	3·04	4·1
3	2·10^{11}	40	25·2	4·46	5·6
3	2·10^{11}	40	16·3	2·94	5·5
4	2·10^{9}	150	0	0·028	0

INTERNAL STANDARD ANALYSIS

Leliaert *et al.*[1–3] have already shown that the use of an internal standard allows a correction to be made for self-shielding effects and neutron-flux irregularities. As the neutron-flux gradient in the neighbourhood of site 4 is quite high, it seemed advisible to use this internal standard procedure. Manganese was therefore added to one of the two irradiated samples. The manganese content is given by

$$\%\,\text{Mn} = \frac{A_{t_0}(\text{Mn}) \times 100}{a \times S_{t_0}(\text{Mn})} \tag{1}$$

where

$$S_{t_0} = \frac{1}{c}\left[A_{t_0}'(\text{Mn})\,.\,\alpha - \frac{b}{a}\,A_{t_0}(\text{Mn})\right], \tag{2}$$

α being given by

$$\alpha = \frac{b}{a}\,\frac{A_t}{A_t'} \tag{3}$$

where

a and b = weight of samples 1 and 2,

c = weight of manganese added to sample 2,

A_{t_0}(Mn) and A_{t_0}'(Mn) = net manganese activity of samples 1 and 2 respectively at time t_0 (end of irradiation),

A_t and A_t' = rest activity of samples 1 and 2 respectively at a time t after complete decay of the manganese activity.

EXPERIMENTAL

Procedure by integral counting

Two steel samples of approx. 300 mg are accurately weighed. With one of the samples a known amount of approx. 5 mg of manganese (as MnAc$_2$·4H$_2$O) is homogeneously mixed. The samples are pressed in pellets of 5·5 mm diameter and a thickness of approx. 3 mm.

The samples are irradiated in the reflector of BR-1, site 4, during a 10-min period. Integral counting, using a well-type NaI(Tl) crystal is started 4 hr after the end of the irradiation. Counting time is 1 min with 30 min intervals. About 24 hr after the end of the irradiation the manganese activity can be considered as negligible, allowing the computation of the correction factor α from the activity of the long living species.

Two typical decay curves (235/I 18–8 and 155) are given in Fig. 3, from which it appears that the analysed half-life of ^{56}Mn is in good agreement with the expected value of 2·58 hr.

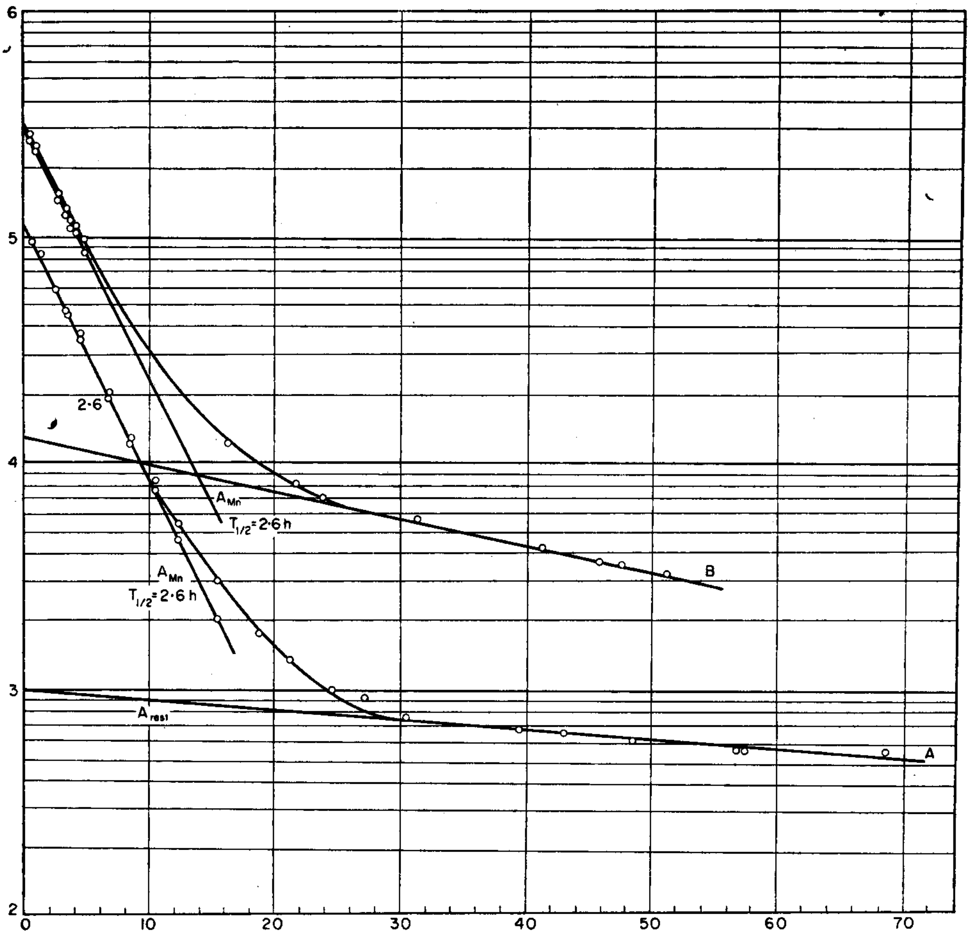

FIG. 3.—Decay curves of steel 235/I and steel 155.
A—231/I, 18/8′
B—155.

Analyses of a number of British Chemical Standard and National Bureau of Standard Steels are summarised in Table III.

From Table III it appears that the results obtained by activation analysis are in excellent agreement with those obtained by careful chemical analysis, giving approximately the same standard error.

Procedure by pulse height discrimination

Steel samples prepared as described above were measured with a well-type NaI(Tl) crystal coupled to a pulse height discriminator and counter. The pulse height discriminator was set to measure only gamma's with energy higher than 1·5 MeV. In this condition ^{56}Mn is measured specifically in the

TABLE III.—ACTIVATION ANALYSIS OF Mn

Sample	% Mn given	% Mn found
BCS 235/1	0·60 ± 0·017	0·608 ± 0·03 (18)‡
NBS 155	1·25 ± 0·015* 1·24 ± 0·01†	1·235 ± 0·027 (16)
NBS 101d	0·739 ± 0·004	0·795 ± 0·008 (12) 0·748 ± 0·014 (9)

* Bismuthate method.
† Persulphate method.
‡ Number of analyses between brackets.
BCS 235/I: 18·3% Cr; 8·21% Ni; 0·36% Ti; 0·6% Si.
NBS 155: 0·485% Cr; 0·517% W; 0·1% Ni.
NBS 101d: 18·68% Cr; 9·05% Ni.

presence of the other activated steel constituents, as appears from the decay curves obtained from different standard steels (see Fig. 4).

About 24 hr or more after the end of the irradiation, the correction factor α is computed from the integral count-rate of the long lived species.

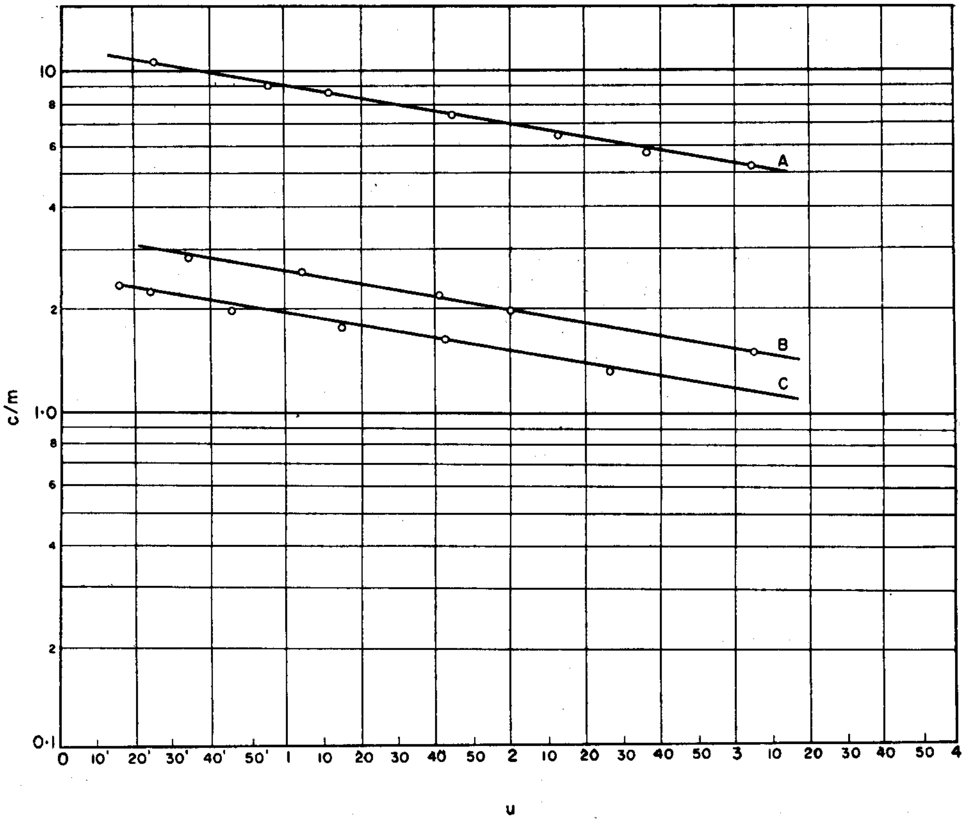

FIG. 4.—Decay curves of ^{56}Mn.
A—PMA 266: $T_{1/2}$ = 2 hr 32 min.
B—NBS 155: $T_{1/2}$ = 2 hr 32 min.
C—NBS 101d: $T_{1/2}$ = 2 hr 37 min.

The results of a series analyses of NBS steel 101d (Mn 0·739%; Cu 0·184%; Ni 9·05%; Cr 18·68%; V 0·049%; Mo 0·11%; Co 0·058%) are represented in Table IV.

TABLE IV. ACTIVATION ANALYSIS OF NBS STEEL 101d

Sample weight, *mg*			α	% Mn
a	b	c		
319·36	312·39	5·232	1·071	0·762
320·25			1·486	0·760
282·10			0·928	0·742
305·83			1·193	0·751
319·36	342·81	5·359	1·091	0·777
320·25			1·512	0·775
282·10			0·944	0·757
305·83			1·214	0·766
319·36	317·86	4·877	1·032	0·747
320·25			1·432	0·745
282·10			0·894	0·727
305·83			1·149	0·736
319·36	268·29	5·115	0·618	0·733
320·25			0·857	0·731
282·10			0·535	0·713
305·83			0·688	0·722

Average: 0·747 ± 0·021
Stand. dev.: 2·8%

Although all samples were irradiated simultaneously in the Lucite container illustrated in Fig. 5, it appears that a considerable variation in the correction factor occurs, since it varies from 0·5 to 1·5.

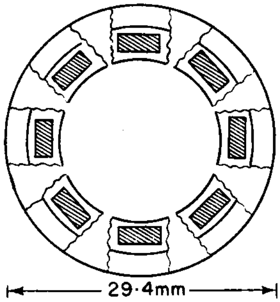

FIG. 5.—Diagram of the Lucite container.

Results of the analyses of other steel standards are represented in Table V, giving evidence that the method is applicable to widely varying steel samples.

The results of Table V appear to have the same accuracy and precision as those obtained by integral counting. In fact, for small manganese contents the standard errors are not larger than those computed from the certificates.

TABLE V. ACTIVATION ANALYSIS OF Mn IN HIGH-ALLOY STEELS

Sample	% Mn given	% Mn found
BCS steel 266 *PMA*		
Co: 23·4% Ni: 13·3% Al: 7·95%	0·27 ± 0·012*	0·276 ± 0·005 (9)†
Cu: 3·3% Ti: 0·1% Fe: 49·7%		
BCS steel 233 *PMA*		
Co: 23·7% Ni: 11·2% Al: 6·98%	0·235 ± 0·005	0·245 ± 0·017 (12)
Cu: 5·09% Fe: 51·15%		
NBS 155		
Cr: 0·485% W: 0·517% Ni: 0·1%	1·25 ± 0·015 1·24 ± 0·01	1·24 ± 0·050 (20)
NBS 101*d*		
Cr: 18·68% Ni: 9·05%	0·739 ± 0·004	0·746 ± 0·021 (16)
BCS cast iron 149		
S: 0·011% P: 0·010%	0·023 ± 0·0018	0·025 ± 0·001 (28)

* Standard deviation from certificates.
† Number of analyses in brackets.

Zusammenfassung—Neutronenaktivierungsanalyse wurde zur Bestimmung von Mangan in Gusseisen und Stählen herangezogen. Selbstabschirmung sowie irregulärer Fluss der Neutronen wurden durch Verwendung eines internen Standards als Fehlerquellen ausgeschaltet. Zwei Methoden, integrale Zählung und Messung der Impulsstärke wurden angewandt. Resultate an Proben mit weit wechselnden Mangangehalten, zeigten vorzügliche Ubereinstimmung mit denen nach klassischen, chemischen Methoden erhaltenen.

Résumé—Les auteurs ont mis au point une méthode d'analyse par activation pour le dosage du manganèse dans la fonte et dans les aciers spéciaux. Les erreurs d'auto-protection et les irrégularités du flux de neutrons sont évitées par l'utilisation d'un étalon interne. Deux procédés sont utilisés: comptage intégral et mesure de la hauteur des impulsions. La méthode a été essayée sur des échantillons étalons. Les résultats obtenus sur des échantillons avec une composition très différente sont en très bon accord avec ceux obtenus par l'analyse chimique classique.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH NITROSO R-SALT

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Summary—A procedure is outlined for the spectrophotometric determination in the visible light region of palladium^{II} with nitroso R-salt. The absorbance of the red organo-palladium complex is measured at 510 mμ; the optimum pH range is 2 to 2·6. The colour reaction is instantaneous, and the complex formed is stable for several days and obeys Beer's law. The tolerance to a number of ions has been established, and palladium can be determined, even in the presence of gold, with good precision and accuracy.

INTRODUCTION

AMONG the various procedures for the spectrophotometric determination of palladium, the method proposed by Cheng[1] using 2-nitroso-1-naphthol seems to be a relatively simple one. This method, however, requires the extraction of the palladium complex into toluene. It seemed to the authors that in order to avoid the extraction step a sulphonic derivative of a similar compound could be used for such a procedure. It is the purpose of this paper to present such a method, using nitroso R-salt (sodium 1-nitroso-2-naphthol-3,6-disulphonate).

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Beckman spectrophotometer model DU, using matched 1·00-cm Corex cells.

All pH measurements were made with a Photovolt glass electrode pH meter model 100.

Reagents

Nitroso R-salt, 0·02*M aqueous solution:* Prepared from B.D.H. material. The solution is stable for several months.

Palladium solution: Dry purified palladium^{II} chloride (Fisher) was dissolved in 0·25*M* hydrochloric acid to give a 0·01*M* solution of palladium. The standardisation was made gravimetrically by precipitating with β-furfuraldoxime.[2] Four analyses were in good agreement and gave an average of 1060 ppm of palladium. The solution was then diluted with distilled water to 0·0002*M* or 21·34 ppm of palladium.

Reagent grade salts were used to prepare solutions of the various other ions.

Absorption spectra

The addition of 1 drop of the reagent solution to 1 drop of palladium solution causes a red colour to be formed at once. In Fig. 1 the absorption spectra of the red coloured complex and of the reagent itself are shown. The maximum absorbance of the complex is at 430 mμ and there is a plateau at 500–510 mμ. Since the reagent itself has a significant absorbance at 430 mμ we preferred to make our measurements at 510 mμ where the absorbance of the reagent is negligible and a water blank is satisfactory.

Effect of pH

The best results were obtained when acetic acid was present at 0·2*M* concentration and the pH was about 2·6 (Fig. 2, curve I). A calibration curve of smaller slope was obtained in the presence of hydrochloric acid at 0·01*M* concentration and the pH was about 2 (Fig. 2, curve II). In cases where

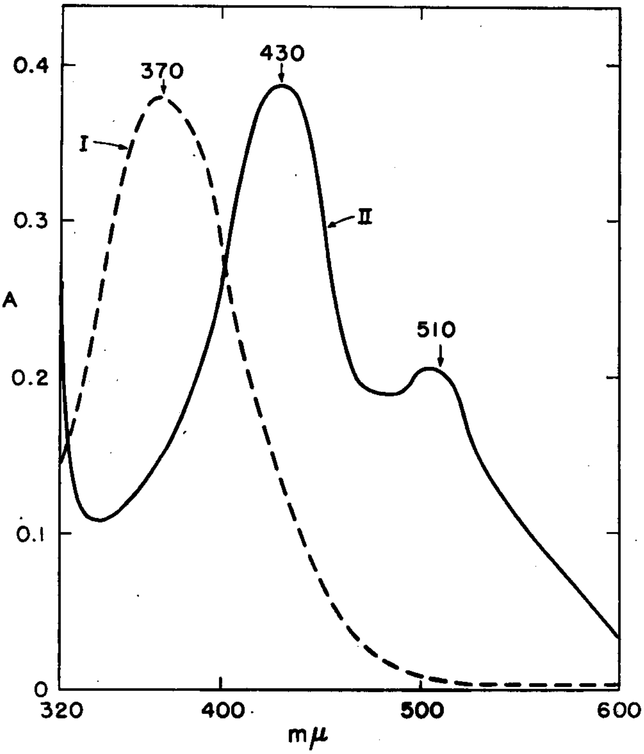

FIG. 1.—Curve I: Spectrum of a solution of nitroso R-salt at a concentration of 6×10^{-4} *M* in water. Length of path, 0·1 cm.
Curve II: Spectrum of a solution of 1·0 ml of 0·0002*M* $PdCl_2$ + 2·0 ml of 0·0002*M* nitroso R-salt + 1·0 ml of 0·1*M* HCl + 6·0 ml of water. Length of path, 1·0 cm.

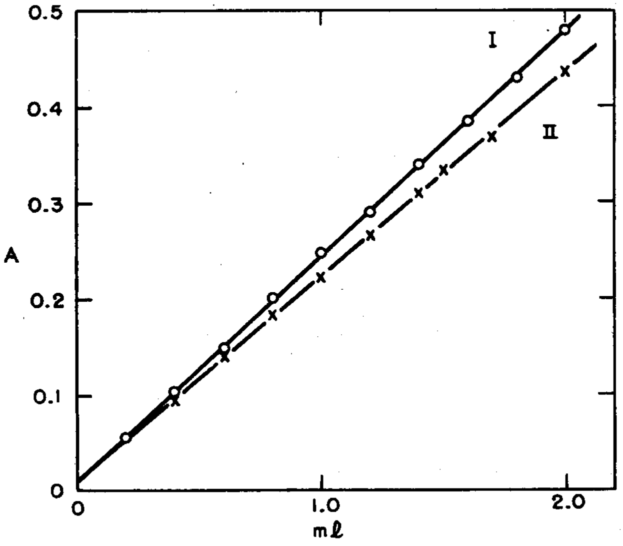

FIG. 2.—Curve I: Calibration curve; absorbances of solutions with 1 ml of 0·002*M* nitroso R-salt + 2 ml of 2*M* CH_3COOH + X ml of 0·0002*M* $PdCl_2$ + (7-X) ml of water.
Curve II: Calibration curve; absorbances of solutions with 1 ml of 0·002*M* nitroso R-salt + 1 ml of 0·1*M* HCl + X ml of 0·0002*M* $PdCl_2$ + (8-X) ml of water.

acetic acid might form complexes with other ions present it would be preferable to use hydrochloric acid.

Concentration of reagent

It is desirable to use an excess of the reagent, since the absorbance of the solution is increased somewhat by increasing the concentration of the reagent. For a sample solution of total volume 10·0 ml, we used 1·0 ml of 0·002*M* nitroso R-salt solution, and the amounts of palladium varied between 0·2 ml and 2·0 ml of 0·0002*M* solution.

Beer's law

In Fig. 2 are represented two calibration curves. In curve I the pH is adjusted by using 2·0 ml of 1*M* acetic acid in a sample of total volume 10·0 ml. The molar absorptivity is $\alpha = 1{\cdot}2 \times 10^4$.

In curve II the pH is adjusted by using 1·0 ml of 0·1*M* hydrochloric acid in a sample of total volume 10·0 ml. The molar absorptivity in this case is $\alpha = 1{\cdot}1 \times 10^4$.

Beer's law is obeyed over the concentration range tested, *viz.*, up to 4·27 ppm of palladium, the most sensitive range being 1·28 ppm to 4·27 ppm, which gives absorbances of 0·141 to 0·450.

Stability

The colour is formed immediately and is constant when measured 15 min after preparation or at any time afterwards within 24 hr.

Tolerance to diverse ions

The interferences of platinum, rhodium, osmium and gold were checked. Solutions which contained 2·13 ppm of palladium and 20 to 40 times as much of the above mentioned elements did not show any significant interference. However, the absorbance of the solutions containing $HAuCl_4$ changed slowly with time. Therefore, the absorbances had to be measured within 1 hr after preparing the solutions. The best results were obtained when a blank solution, containing the same materials except for palladium, was prepared simultaneously. By doing so the differential absorbance was constant over a period of almost 2 hr. When other elements were present the absorbance could be measured even after 1 day.

DISCUSSION

The use of nitroso R-salt for the determination of small amounts of palladium has several advantages. The complex formed is soluble in water, and no extraction is required; the colour reaction is rapid and is stable; the stock solution is stable over a long period of time; the pH for maximum absorbance is easily controlled. It allows a high tolerance for several ions, and this is most important in the presence of gold, which, when using other methods, has to be removed before the determination of palladium. It is a rapid, sensitive, and precise method. Since the colour of the complex is red, the method can probably be easily adapted for colorimetric determinuoı̣ʇɐ.

Zusammenfassung—Eine Methode zur spectrophotometrischen Bestimmung von Palladium(II) mit Nitroso-R-Salz im sichtbaren Bereich wird mitgeteilt. Die Absorption des roten Palladiumkomplexes wird bei 510 mμ gemessen. Der optimale pH-Bereich ist 2-2·6. Die Reaktion verläuft momentan, die Farbe ist über Tage hinaus beständig und Beer's Gesetz ist erfüllt. Der Einfluss einiger Ionen wurde studiert. Palladium kann selbst in der Gegenwart von Gold genau bestimmt werden.

Résumé—Les auteurs donnent un aperçu d'un procédé de dosage spectrophotométrique dans le visible du palladium II par le sel nitroso-R. L'absorption du complexe organique rouge du palladium est mesurée à 510 mμ; le domaine de pH le meilleur est 2-2,6. La réaction colorée est instantée, le complexe formé est stable pendant plusieurs jours et obéit à la loi de Beer. La tolérance pour un certain nombre d'ions a été établie, le palladium peut être dosé avec une bonne précision, même en présence d'or.

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NEW METHODS OF INORGANIC ULTRAMICROANALYSIS UNDER THE MICROSCOPE

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Summary—The results of investigations carried out by the authors in the field of ultramicroanalysis on the stage of a microscope are presented. The peculiarities of ultramicromethods are considered in detail, and the new techniques of experimentation in qualitative and quantitative ultramicroanalysis are described: electrolysis with platinum and mercury electrodes, potentiometric and amperometric titration, and separation of metals by means of ion-exchange resins. The results of the determination of a number of elements by various ultramicroanalytical methods are given.

ULTRAMICROCHEMICAL analysis is a comparatively new development in analytical chemistry which enables the problem of investigating very small amounts of substance to be solved.

There are now two trends in ultramicroanalysis, depending on the quantities of substance investigated, which determine the manipulative technique. On the one hand, simple mechanical devices are used when manipulating with volumes of n × 10^{-3} ml, and the majority of chemical procedures are observed with the unaided eye or with the aid of a magnifying glass; on the other hand, with volumes less than 10^{-3} ml, all the main chemical procedures are carried out on the stage of a microscope with the use of micromanipulators. The practical techniques of experimentation for the first trend have been developed by P. Kirk's (U.S.A.), and I. Korenman's (U.S.S.R.) schools.

The most general apparatus for chemical experimentation on the stage of a microscope with the use of micromanipulators, and the technique of working, became known due to the work carried out by A. A. Benedetti-Pichler and his co-workers (U.S.A.). Later this trend has been fruitfully developed by C. L. Wilson's (Gt. Britain) school.

The aim of our investigations was the further development of the technique and methods of experimentation for this trend, to make possible the use on this scale of the most widely used methods of analysis. We considered it expedient to choose this particular trend for systematic study from the point of view of utilising more completely the possibilities of the ultramicromethod for the investigation of small samples.

PECULIARITIES OF THE ULTRAMICROMETHOD OF CHEMICAL ANALYSIS

Chemical determinations with small amounts of material can be carried out by ultramicroanalysis, while maintaining the usual concentrations of the reacting substances, by decreasing the volume of the solution correspondingly. This results in the increase (in comparison with the macro method) of the relative surface of the solution and the vessel, *i.e.* in the increase of surface per unit volume, owing to the fact that surface decreases to a lesser degree than volume. This is shown in Table I.

Because of the relatively greater area of contact with the walls of the vessel, dissolved substances are adsorbed by these, and attack the walls to a greater extent than in the macro method.

TABLE I.—RATIO OF RELATIVE SURFACES

Method	Diameter of the vessel, *cm*	Height of the vessel, *cm*	Surface of the vessel, *cm*^{2}	Volume of the solution, *cm*^{3}	Relative surface, S	$\frac{S_u}{S_m}$
Macro method	4·0	4·0	62·5	50·0	1·25	>20
Ultramicro method	0·2	0·2	0·16	0·006	26·6	

When working on the ultramicro scale, the free surface of liquid is also relatively larger, because of the curvature of the meniscus in capillaries.[1] So the speed of evaporation of solutions, which is directly proportional to the free surface of liquid, reaches a considerable value. Obviously, liquids moistening a capillary have a considerably lower vapour pressure in it than in wide vessels, because of the larger curvature of the concave surface. Nevertheless, the evaporation goes on much faster, since the relative increase of the free surface is considerably larger than the decrease of vapour pressure. For example, the free surface of liquid in a capillary of 0·6 mm diameter is not equal to 0·3 mm^2, as is the flat surface, but is about 0·6 mm^2, whereas the vapour pressure above the meniscus of the corresponding curvature decreases only by 5%. In addition, the solution in a capillary is in considerably better condition from the point of view of heat transfer. In order to diminish the speed of evaporation of liquids from capillaries, a method of working in a humid atmosphere is used; in this case the speed of evaporation from comparable volumes decreases by 10–15 times.

Aqueous solutions of salts, having lower vapour pressure than water, evaporate, other things being equal, more slowly than water, but not to such a degree that the necessity of working in a humid atmosphere is eliminated. When working in a humid atmosphere, the volume of saturated salt solutions increases because of the equalisation of vapour pressure in the system, Vapour above pure water (humid atmosphere)—Vapour above a saturated solution in a capillary. The hygroscopicity of the dissolved compound is also of importance. For example, comparable volumes of a saturated calcium chloride solution in a humid atmosphere increase about 30 times faster than in a normal atmosphere. Therefore it is not advisable to work with saturated solutions of salts and concentrated acids in a humid atmosphere.

The relative increase of the surface of a liquid in comparison with its volume results in an increase of adsorption of substances from solutions and of the speed of evaporation as well as in an increase of surface tension, which reaches considerable values when working in capillaries. This must be taken into consideration first of all when the experimental technique for an ultramicromethod is being developed. On the one hand, the situation is more complicated because of the necessity of overcoming the surface tension when the liquid is transferred from one capillary to another. On the other hand, this eliminates losses of the solution through spilling, and permits the exact measurement of solutions, because of the stable (within the limits of the speed of evaporation) position of the meniscus.

Solutions of salts, as is known, have a greater surface tension than water; the tension increases almost in proportion to the number of equivalents of the dissolved salt. The creeping of salts (for example, ammonium chloride), which is a serious hindrance when working in capillaries, can be explained by the increase of surface tension.

To eliminate, to a considerable degree, a number of the effects connected with the large surface of contact of the solution with the walls of the vessel, and with the use of capillaries, we suggest coating the walls of a micro vessel by a layer of an organosilicon compound.[2]

The glass surface coated with a methylchlorosilane film is not moistened by water solutions; this makes possible manipulation with them without washing the vessel. When working with such vessels the titration error connected with the speed of the solution flowing out of a horizontal burette is reduced to zero.

The hydrophobic surface is poorly moistened by water solutions because of the decrease of surface tension on the border between this surface and the solution. This is why such phenomena as the creeping of salts to the outside walls of capillary vessels, and of calomel micro electrodes, can be eliminated by making them hydrophobic (Fig. 1*a*).

The free surface of liquid in capillary vessels treated with the solution of an organosilicon compound decreases considerably owing to the flattening of the meniscus (Fig. 1*b*). Because of this, the speed of evaporation from such vessels decreases considerably (approximately by 25%). In addition, the measurement of volumes in burettes and vessels using the flat meniscus is more simple and accurate.

Owing to the greater value of the $\frac{S}{V}$ ratio in the ultramicro method, special attention must be paid to the possibility of losing the substance by adsorption, even from solutions of usual concentration. Investigations carried out with radioactive isotopes showed that losses of substance by adsorption are considerably less when working in vessels with hydrophobic walls.

Special consideration must be given to the problem of observation of the colour of solutions in coloriscopic capillaries.[1] A mean sensitivity for a number of colour reactions is 10^{-8} g in 1 ml. In ultramicro methods (with volumes of 10^{-3}–10^{-4} ml) the sensitivity may be as high as 10^{-12} g.

Assuming that the Bourguer-Lambert-Beer law, $E = kcl$, is valid for immeasurably small concentrations of substance, a minimum concentration for a certain reaction should be quoted only in a layer of a given thickness. Only in this sense has the notion of "minimum concentration" a precise meaning.

For a given coloured substance ($K = \text{const.}$) the product $cl = E$ is constant. It follows that the minimum concentration value is determined by the nature of the coloured substance and the chosen length of the light path; it does not depend on other values, in particular, on the cross-section of the layer of liquid.

The sensitivity of a reaction, in addition to the minimum concentration, is determined also by the identified minimum

$$m = c_{\min} \cdot v = c_{\min} \cdot \underset{\text{chosen}}{l \cdot s},$$

that is, the identified minimum is proportional to the cross-section of the layer of liquid.

The thickness of the layer of a coloured solution in coloriscopic capillaries is comparable with that in the macro method, whereas the cross-section is considerably less. This makes it possible essentially to decrease the identified minimum. The cross-section of the layer of liquid in the ultramicromethod is usually 10^{-4} times that in the macro method. Hence, the detected minima of elements determined are in the same ratio.

The limiting concentration per unit length, which does not depend on the cross-section of the column of liquid, when the layer thicknesses are comparable, is the same for the macro and ultramicro method.

It has been confirmed by our experimental results that the identified minimum depends on the cross-section of the layer of a coloured solution. Thus, in the macro method when the cross-section of the solution layer is 1 cm^2, the identified minimum for iron is 10^{-5} g, whereas in the ultramicro method it is 10^{-9} g.

QUALITATIVE AND QUANTITATIVE ULTRAMICROANALYSIS

According to the literature, there are now a number of methods and suitable apparatus for qualitative and quantitative analysis on the stage of a microscope.

No attention, however, has been paid to chromatographic separation in small volumes, to electrochemical methods of separation and determination, or to the physicochemical determination of the end-point in titration. This limits the possibilities for investigation by an ultramicrochemist of small amounts of substance.

The following is the description of some new apparatus and methods for analysis on an ultramicro scale.

Chromatographic separation in small volumes

Chromatographic separation used as an ultramicro method has a great advantage over other methods of separation, because the separated elements can be often obtained in a very pure state without introducing into the solution a reagent which is difficult to remove. As well, the process of separation on the ultramicro scale takes considerably less time because of working with small volumes of solutions and the use of small amounts of sorbent (0·05–0·1 g).

The ultramicro technique of chromatographic experimentation has no difference in principle from the usual one. But the work with small volumes inevitably affects the apparatus and the methods of manipulation.

We propose the use for this purpose of a column which consists of a thin-walled capillary of 2 to 2·5 mm diameter and 3 to 4 cm long with a drawn out end and a porous glass partition. The solution is forced out of the column by the pressure created by a levelling bulb. The eluates are collected in microvessels of 1·5 to 2·0 mm diameter. The vessels are placed in a circle on a rotating cylindrical stand-holder. Solutions are introduced into the column by a micropipette (Fig. 2).

Iron and nickel, chromium and vanadium were separated by this method in volumes of $1{\cdot}2 \times 10^{-3}$ ml in quantities of $0{\cdot}5 \times 10^{-6}$ to 1×10^{-6} g.

Electrochemical separation and identification of elements

Electrochemical analysis under the microscope can be carried out by means of the special apparatus constructed by the authors.[3]

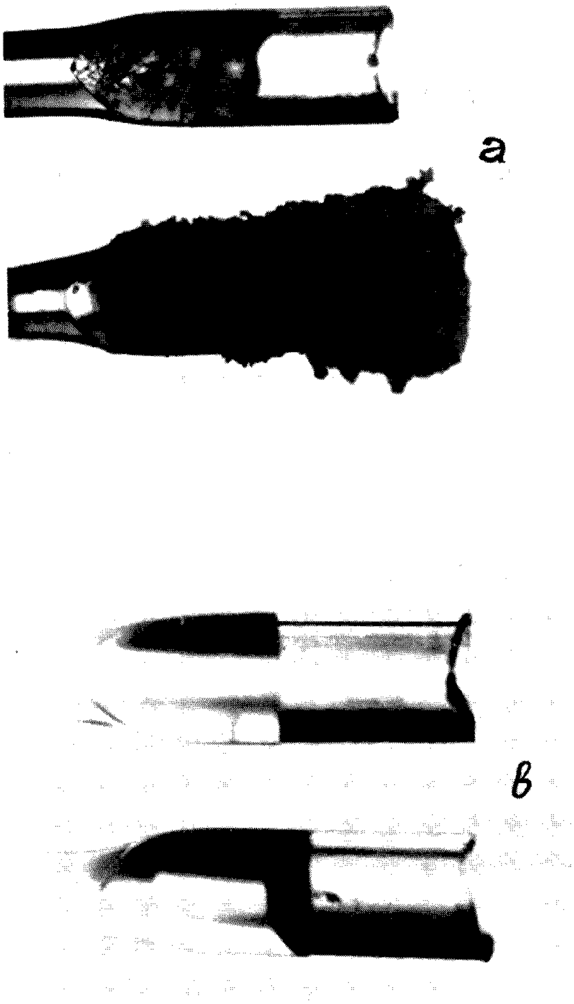

FIG. 1.—Effect of hydrophobisation of the walls of micro vessels.

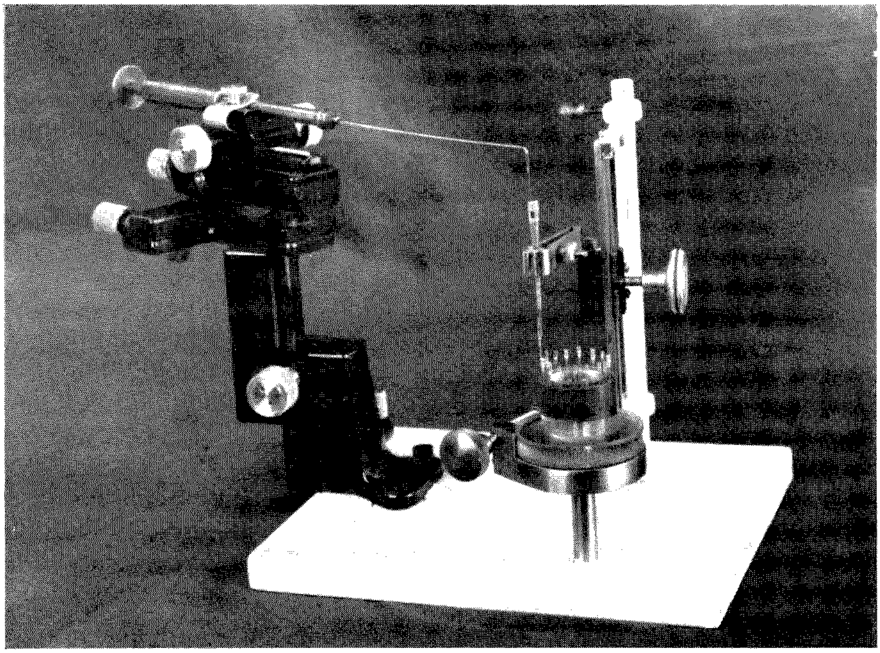

FIG. 2.—Chromatographic column (1/3–1/4 natural size).

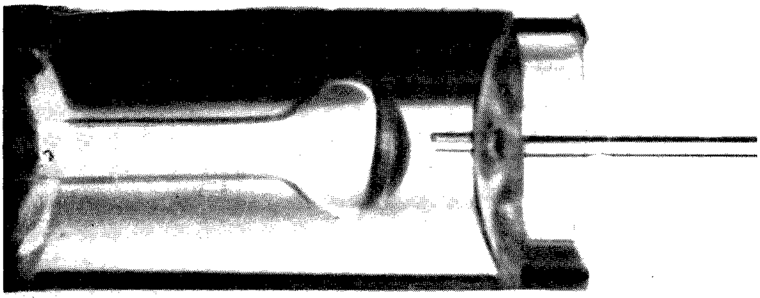

FIG. 7.—Microcell with a glass electrode.

For obtaining a certain current density (0·1–0·01 A/cm^2) it is necessary to have a current strength of 10^{-4} to 10^{-5} A, because of the small surface of the electrodes used in the ultramicro method. The apparatus is different from that for macro electrolysis (a micro cell is used).

The cells used for electrolysis with platinum electrodes were of two types:

(a) The electrolyte is placed on a platform in a thick-walled capillary in the form of a condenser rod which has a platinum wire about 0·2 mm in diameter welded into its channel; the end of the wire which is in the platform plane serves as the anode.

The cathode consists of a platinum wire welded to a flexible wire which passes through the capillary and the ebonite holder. There is a terminal at the end of the flexible wire to connect to the source of current (Fig. 3*a*).

(*b*) The electrolyte is placed in a microvessel into which the platinum electrodes are inserted. The electrodes consist of isolated platinum wires 0·1–0·2 mm in diameter welded into a capillary. The electric current is fed through thin flexible wires one end of which each of these being welded to the platinum wire and the other to the terminals of the ebonite holder (Fig. 3*b*).

Using the apparatus described, it is possible to isolate and identify 10^{-6}–10^{-8} g of a metal in a volume of 10^{-3}–10^{-4} ml, the electrode surface being equal to about 10^{-4} cm^2.

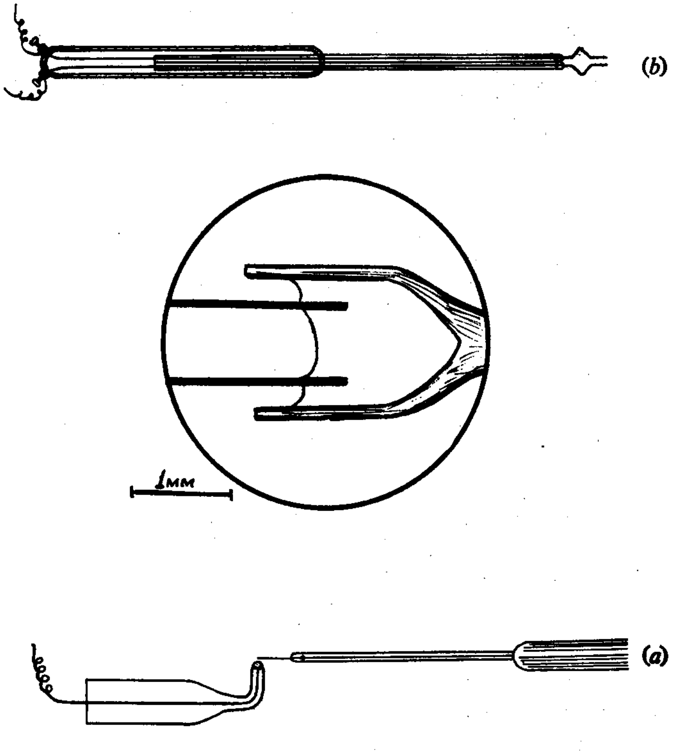

FIG. 3.—Electrolytic micro cells with platinum electrodes.

Electrolysis on a mercury cathode is carried out in a capillary with both ends open because of the intense gas-generation during the electrolysis, because of which the solution is ejected from an ordinary vessel.

The mercury cathode is made by electrodepositing mercury on a platinum fork which serves as cathode in the electrolysis (Fig. 4).

After deposition of the metal on the mercury cathode, the mercury may be removed by connecting the cathode in the circuit to a micro heater. Mercury having been removed, the metal remaining on the fork is dissolved by immersing in a suitable solvent in a micro cone, and it is then identified in the solution by a sensitive reaction.

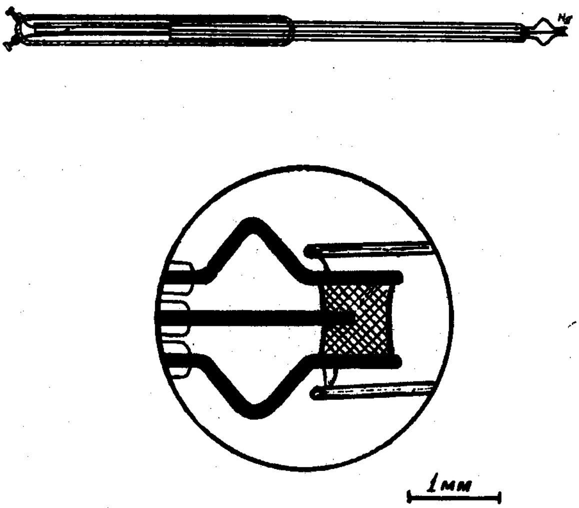

FIG. 4.—Mercury micro cathode.

It is possible to deposit 10^{-6}–10^{-7} g of a metal on a mercury cathode of 2×10^{-3} cm^2 surface from a volume of solution of about 10^{-3} ml, in 15–20 min.

Some of the results of the qualitative identification of a number of elements obtained during the development of the method are given in Table II.

TABLE II.—QUALITATIVE IDENTIFICATION OF SOME ELEMENTS

Element	Reagent	Limit of identification, *g*	Method of identification
Ag	Potassium chromate	1×10^{-9}	Microcrystalloscopy
Fe	Potassium thiocyanate	2×10^{-9}	Coloration in the coloriscopic cuvette
Cr	Diphenylcarbazide	3×10^{-12}	Coloration in the coloriscopic cuvette
Ni	Dimethylglyoxime	1×10^{-8}	Precipitate
Cu	—	5×10^{-8}	Electrolysis
Pb	—	5×10^{-7}	Electrolysis

Titrimetric ultramicroanalysis

More precise titration and decrease in the drop error is possible in ultramicrotitration by using electrometric methods for the determination of the equivalent point.

But the wide use, for example, of *potentiometric titration* in ultramicro titrimetric analysis is hindered by a number of specific difficulties in connection with the investigation of very small volumes.

We recommend, as a cell for potentiometric titration, a capillary vessel of 1–2 mm diameter with a platinum wire welded into it, and a reference calomel electrode with a capillary end. The burette is also a capillary of about 0·5-mm bore, the end of which is drawn down to 0·02 mm in diameter. Such a burette works as a micropipette, but with the possibility of the exact measurement of solutions. To carry out the measurement a dial micrometer placed between the micrometer screw and the holder, of which the moving part works as a plunger, is used. In this case, a certain number of scale divisions, recorded by the micrometer scale pointer when the screw is turned, corresponds to a certain volume of solution when the burette is filled or emptied. This volume is easily measured by calibrating the burette.

The mixing of solution during the titration can be suitably performed by a nitrogen current which is fed through a tube with a capillary end directed to the surface of the liquid. The gas current causes turbulent motion of the liquid in the vessel.

To carry out the titration, a vessel with the indicator electrode, and a holder with the necessary vessels, are placed into the moist chamber on the stage of the microscope. The burette, the calomel electrode, and the tube to feed the mixing gas, are clamped in three manipulators placed to the right of the microscope (Fig. 5). Turning the vessel to each of the manipulators in succession, the titrant is added, the solution is mixed, and the potential value is measured. Titrating 0·5–1·5 × 10^{-3} ml with 0·1–0·01*N* solutions, 10^{-6}–10^{-7} g of an element can be determined with an accuracy of 0·5–3 %.[4]

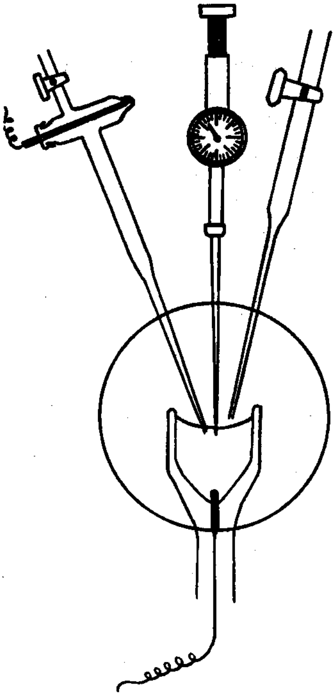

FIG. 5.—Cell for potentiometric ultramicro titration.

For *amperometric ultramicro titration* on the stage of the microscope, the following apparatus and method are used. The indicator electrode is a vibratory platinum wire, 0·2 mm in diameter and 2–3 mm long. The reference electrode is a saturated calomel electrode with a capillary end.

Titration can be suitably performed in a capillary microvessel, and the titrant can be added by the burette with a dial micrometer screw.

The micro vessel on the holder is placed on the stage of the microscope in a moist chamber with a cross slot in its side wall. Through this slot a vibratory electrode is inserted into the chamber. The electrode is set in the clamp of the manipulator perpendicular to the two other manipulators which are placed, as usual, to the right and the left of the microscope. The burette and the reference electrode, with ends bent to a right angle, are clamped in these manipulators (Fig. 6). As the titrant is added, the galvanometer deflection is recorded, and the corresponding volume of the titrant is measured by the burette scale. From 10^{-7} to 10^{-8} g of an element can be determined amperometrically in 0·5–1·5 × 10^{-3} ml of 0·01–0·001*N* solution. The accuracy of the determination is about 1 %.[5]

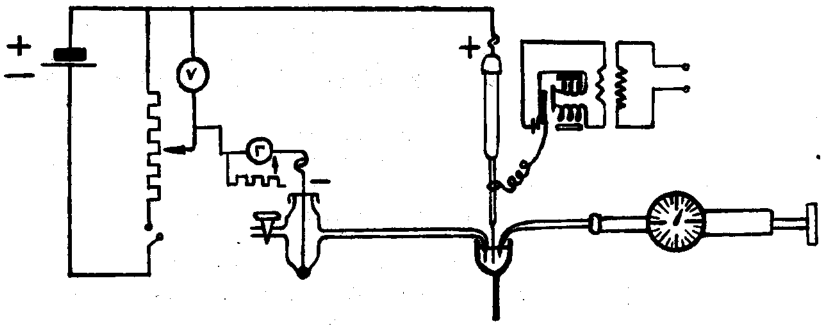

FIG. 6.—General diagram of the apparatus for amperometric ultramicro titration.

A glass electrode with a bulb about 0·3 mm in diameter, made in the microflame of a special glass capillary, is used for *measuring the pH* of solutions in volumes of about 10^{-3} ml. The glass and calomel electrodes are placed in the right and left manipulators, brought into the field of vision of the microscope, and immersed in the solution contained in the section of the capillary on the microscope stage (Fig. 7). Tests of such a micro cell with buffer solutions, in comparison with measurements made using a standard cell, showed a satisfactory reproducibility of pH values within 1–3% of the value measured.

The results of some quantitative determinations carried out by means of the methods developed, are given in Table III.

TABLE III. QUANTITAVE ULTRAMICRO DETERMINATIONS

Element	Taken, *g*	Found, *g*	Error %	Method
Cr	$1·73 \times 10^{-7}$	$1·733 \times 10^{-7}$	+0·2	Potentiometric titration
Fe	$0·56 \times 10^{-6}$	$0·57 \times 10^{-6}$	+2·0	
V	$5·1 \times 10^{-7}$	$5·22 \times 10^{-7}$	+2·3	
Cl	$3·3 \times 10^{-7}$	$3·27 \times 10^{-7}$	−1·0	
V	$2·55 \times 10^{-8}$	$2·53 \times 10^{-8}$	−0·8	Amperometric titration
V	$5·2 \times 10^{-8}$	$5·24 \times 10^{-8}$	+1·0	
Mg	$5·5 \times 10^{-9}$	$5·8 \times 10^{-9}$	+7·0	Colorimetry
S	$7·7 \times 10^{-8}$	$8·08 \times 10^{-8}$	+5·0	
K	$3·3 \times 10^{-8}$	$3·1 \times 10^{-8}$	−6·0	By the volume of the precipitate

In conclusion we should like to add that the techniques of experimentation either known before or described here have been used to investigate various small samples (inclusions and very small parts of meteorites, cell sap of plankton diatoms,[6] various thin coatings, corrosion products *etc.*)

This has shown that the analysis of small amounts of substance can be carried out on the stage of a microscope. The investigation may be as complete as the investigation of large quantities of substance on the macro scale.

In addition, ultramicro methods may be applied to the analysis of any materials for impurities, on condition that a method for removing the main component (or for isolating the admixtures) is found, which will permit concentration of the admixtures in a small volume.

Zusammenfassung—Neue Geräte und Techniken wurden entwickelt um einige Ultramikroanalysen durchzuführen. Es wurde gezeigt, dass die Analysen unter einem Mikroskop durchgeführt werden können. Die Analysen können genau so komplet sein wie solche, die im Makromasstab vollzogen werden.

Résumé—Les auteurs ont mis au point un appareil et des techniques expérimentales pour un certain nombre de méthodes ultramicrochimiques. Ils ont montré que l'analyse de faibles quantités de substance peut être réalisée à l'aide d'un microscope. Cette étude peut être aussi complète que l'étude de quantités importantes de substances à grande échelle.

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APPLICATIONS OF COMPLEMENTARY TRI-STIMULUS COLORIMETRY—III

THE DETERMINATION OF INDICATOR CONSTANTS AND THEIR USE IN THE CALCULATION OF SCREENING CONDITIONS

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Summary—It is shown that the indicator constants of acid-base indicators can be calculated from complementary tri-stimulus data. It is pointed out that this approach is applicable to the study and evaluation of similar equilibria. From complementary tri-stimulus data for an acid-base indicator and for a screening dye (or dyes) and the calculated indicator constant, the composition of a satisfactorily screened indicator stock solution can be calculated. Examples are given and derived values are compared with experimental results.

THE screening of indicators is an important approach to improving the detectability of end-points. In the past, the proper ratio of an indicator to the screening dye (or dyes) has always been established by trial and error. In a previous paper,[1] it has been shown that complementary tri-stimulus colorimetry permits the calculation of that ratio when the complementary colour co-ordinates of an indicator and of the screening dyes are known, as well as the optical concentration of their stock solutions. In order, for example, to screen the end-point in an acid-base titration at a certain pH value, a solution containing the necessary amount of indicator is brought to that pH value, the absorbance curve is determined, and the complementary colour parameters are calculated.[1]

As will be shown in the present paper, the screening conditions at any pH value within the transition interval of a particular pH indicator can be calculated when the indicator constant and the complementary colour parameters of the indicator in both the acid and base form are known. Further, the indicator constant itself can be calculated from complementary colour parameters.

Determination of indicator constants

From the formula for the dissociation constant of an indicator acid, HI,

$$K_a = K_{in} = \frac{[H^+][I^-]}{[HI]}, \tag{1}$$

the following equation can readily be derived where q is the mole fraction of the indicator in the acid form

$$K_{in} = [H^+] \cdot \frac{1-q}{q}. \tag{2}$$

By bringing equation (2) into the form of its negative logarithm, thus allowing the introduction of the parameters pK_{in} and pH, the following is obtained

$$pK_{in} = \text{pH} - \log\left(\frac{1}{q} - 1\right). \tag{3}$$

This equation holds not only for indicator acids but also for indicator bases, as can be shown by applying the usual definition for the indicator constant of an indicator base, $K_{in} = K_b/k_W$, where K_b is the dissociation constant of the indicator base and k_W is the ionic product of water.

In the first paper of this series[2] it was shown that the mole fraction of a binary mixture of colorants can readily be calculated from complementary colour parameters. In general, the following equation may be used

$$Q_{r,in} = \frac{qQ_{r,m}E_a + (1 - q)Q_{r,b}E_b}{qE_a + (1 - q)E_b}, \tag{4}$$

where Q_r, are the co-ordinates of the complementary colour point (being represented by u, v, and w for $r = 1, 2$, and 3 respectively). E is the overall absorptivity, and the subscripts m, a and b apply to the colorant mixture, and to substances a and b, respectively. In the present case a and b may be assigned, respectively, to the acid and base form of the indicator.

It should be pointed out, however, that the treatment given here for an indicator can be applied equally well to any analogous dissociation equilibrium involving coloured components. Further, it should be recognised that the concept "colour" is used in the broadest sense, since wavelengths may be selected outside the visible region of the spectrum if relation to the human eye need not be maintained. This was demonstrated in the first paper of this series.[2]

By arrangements of terms, equation (4) may be solved for q.

$$q = \frac{E_b(Q_{r,b} - Q_{r,m})}{E_a(Q_a(Q_{r,m} - Q_{r,a}) + E_b(Q_{r,b} - Q_{r,m})}. \tag{5}$$

By taking the reciprocal of equation (5), separating the fraction, and transposing, the following equation is obtained:

$$\frac{1}{q} - 1 = \frac{E_a}{E_b} \times \frac{Q_{r,m} - Q_{r,a}}{Q_{r,b} - Q_{r,m}}. \tag{6}$$

The left side of this equation is exactly the argument of the logarithmic term of equation (3), and its equivalent may be introduced into equation (3) to yield

$$pK_{in} = \text{pH} - \log\left(\frac{E_a}{E_b} \times \frac{Q_{r,m} - Q_{r,a}}{Q_{r,b} - Q_{r,m}}\right). \tag{7}$$

This equation indicates clearly that for the calculation of the indicator constant, only the absorbance curves of the two limiting acid and base forms of the indicators for a transition, and of a mixture of these forms (*i.e.*, at a pH in the transition interval), need be known. From these three curves all the necessary complementary colour parameters can be calculated in the manner previously reported.[1,2]

In order to calculate the E values, the analytical concentration of the indicator must be known. However, for the pure acid form and the pure base form of a particular indicator solution, the molar concentration is generally the same. Employing the definition

$$J = CEl, \tag{8}$$

where C represents the molar concentration, J the optical concentration and l the length of the light path through the solution, it follows that

$$\mathrm{p}K_{in} = \mathrm{pH} - \log \left(\frac{J_a}{J_b} \times \frac{Q_{r,m} - Q_{r,a}}{Q_{r,b} - Q_{r,m}} \right). \tag{9}$$

The application of this approach and of equation (9) can be best appreciated through a practical example, namely, the determination of the indicator constant of tetrabromophenolphthalein. In Fig. 1 are shown the absorbance curves of this indicator as the base form, the acid form, and somewhere in the transition interval (actually at pH = 3·75). The concentration of the indicator was not determined and the solution was made up in such a way that reasonable absorbance values would result. By employing the ten selected ordinate method and the mode of calculation previously described,[1] (*i.e.*, with reference to the human eye), the complementary colour parameters for the three colorants given in Table I were obtained.

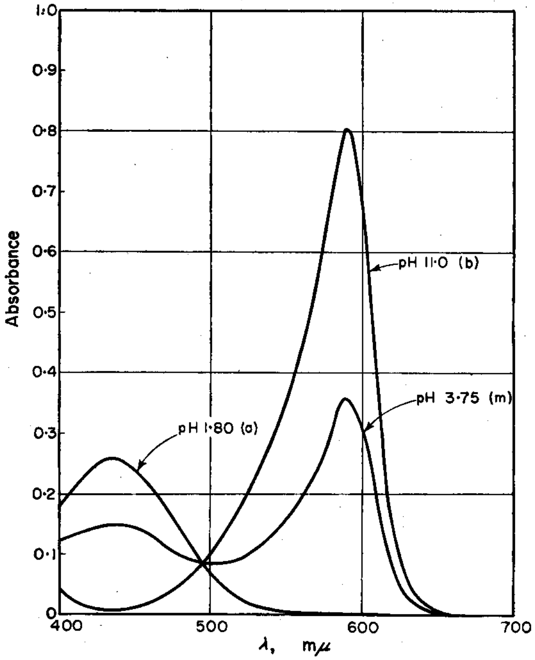

FIG. 1.—Absorbance curves of tetrabromophenolphthalein at various pH values (1-cm cell).

Formula (9) is actually equivalent to three equations in which Q_r becomes successively u, v, and w for $r = 1, 2$ and 3. Inspection of this equation reveals that differences of the particular co-ordinates are involved. Hence, the form of this equation should be employed for which the greatest numerical differences will result; in this way the highest accuracy can be secured. The w co-ordinate was selected for the present example in this way. By substituting in equation (9), the result is

$$pK_{in} = 3{\cdot}75 - \log\left(\frac{0{\cdot}227}{0{\cdot}539} \times \frac{0{\cdot}303 - 0{\cdot}794}{0{\cdot}046 - 0{\cdot}303}\right) = 3{\cdot}8_3.$$

The value for $pK_{in} = 3{\cdot}8_3$, thus obtained, is in good agreement with the value, 3·8, accepted in the literature.[3]

Although in this example the ten selected ordinate method was used, it should be emphasised that reference to the human eye is unnecessary, because the value of the indicator constant is unrelated to the observer's vision. Any suitable number of wavelengths (even one wavelength only in each range) could have been selected appropriately in the visible or non-visible portion of the spectrum.

TABLE I.—COMPLEMENTARY COLOUR PARAMETERS FOR TETRABROMOPHENOLPHTHALEIN

	u	v	w	J
Acid form	0·152	0·053	0·794	0·227
Base form	0·462	0·492	0·046	0·539
Mixture, pH 3·75	0·356	0·341	0·303	0·367

In exactly the same manner pK_{in} for methyl orange and for cresol red were determined. The respective values, $3{\cdot}4_6$ and $8{\cdot}1_4$, are in good agreement with the values 3·5 and 8·1 accepted in the literature.[3] Multi-step indicator equilibria (or any other analogous dissociation equilibria) can be treated in the same manner, provided that the constants for each step are sufficiently different in magnitude to allow neglect of other steps in the consideration of a single step. Thus, for a pH indicator such as thymol blue, which has two transition intervals, both indicator constants can be calculated, but five absorbance curves are needed: one of the form existing in strongly acidic medium; one in the first transition interval; one of the intermediate form; one in the second transition interval, and one of the form present in strongly alkaline solution. Then equation (9) is applied twice, taking into consideration that in the calculations the intermediate form represents the base form in relation to the first indicator constant, and the acid form in relation to the second indicator constant.

Employing the ten selected ordinate method, the values of $pK_{in,2}$ was found to be $8{\cdot}9_2$ which is in excellent agreement with the value 8·9 reported in the literature for thymol blue[3]. However, the value for $pK_{in,1}$ thus obtained differed considerably from accepted values. The obvious reason for this discrepancy was that the solution with the lowest pH (0·8) measured was not sufficiently acid to ensure the exclusive presence of the acid form. Instead of measuring the absorbance curve of an even more acidic solution, the possibility of calculating the complementary colour parameters for this form without ensuring its exclusive presence was investigated. It was found that this could be accomplished as described below.

Assume that the base form (*i.e.*, the intermediate form in the present case of thymol blue) is obtainable and that its complementary colour parameters have been determined; and further, that the absorption spectrum of the mixed acid-base system is known at two different pH-values in the transition interval. Then, since the indicator constant is indeed constant, the following relation exists

$$\mathrm{pH}_1 - \log\frac{J_a}{J_b} \times \frac{Q_{r,m,1} - Q_{r,a}}{Q_{r,b} - Q_{r,m,1}} = \mathrm{pH}_2 - \log\frac{J_a}{J_b} \times \frac{Q_{r,m,2} - Q_{r,a}}{Q_{r,b} - Q_{r,m,2}}, \tag{10}$$

where the subscripts 1 and 2 refer to the parameter of the system at the two different pH values. Equation (10) can be solved for the unknown complementary colour co-ordinates of the acid form, $Q_{r,a}$, to yield

$$Q_{r,a} = \frac{(Q_{r,b} - Q_{r,m,2})Q_{r,m,1} - \dfrac{[H^+]_2}{[H^+]_1} \times (Q_{r,b} - Q_{r,m,1})Q_{r,m,2}}{(Q_{r,b} - Q_{r,m,2}) - \dfrac{[H^+]_2}{[H^+]_1}(Q_{r,b} - Q_{r,m,1})}. \tag{11}$$

Thus the numerical values of the complementary colour co-ordinates of the acid form can be secured even though they were not directly available by experimentation. These co-ordinates can now be employed to calculate the optical concentration of the acid form, J_a, in the following manner. The argument of the logarithm in equation (9) is equal to $(1/q - 1)$. Further, q can be calculated from the following equation

$$J_m = qJ_a + (1 - q)J_b, \tag{12}$$

where J_m is the optical concentration of the mixed form (at either of the two pH values). From equation (12) an expression for $(1/q - 1)$ can be derived, namely

$$\frac{1}{q} - 1 = \frac{J_a - J_m}{J_m - J_b}. \tag{13}$$

This equation may be combined with equation (6), with the E values replaced by the J values according to equation (8), to yield

$$\frac{J_a}{J_b} \times \frac{Q_{r,m} - Q_{r,a}}{Q_{r,b} - Q_{r,m}} = \frac{J_a - J_m}{J_m - J_b}. \tag{14}$$

From this equation by solving for J_a, the following is obtained

$$J_a = J_b \times J_m \frac{Q_{r,m} - Q_{r,b}}{J_m(Q_{r,m} - Q_{r,a}) - J_b(Q_{r,b} - Q_{r,a})}. \tag{15}$$

The reliability of this derivation was established by its application to the determination of the complementary colour parameters of the intermediate (yellow) form of thymol blue, which can readily be obtained from experimental data. The necessary data are given in Table II. Since the study is not related to the human eye, the ten selected

TABLE II.—COMPLEMENTARY COLORIMETRIC PARAMETERS OF THYMOL BLUE IN ITS YELLOW AND BLUE FORM AND THEIR MIXTURES

	u	J
Strong base	0·105	4·12
Acid (pH 5)	0·572	4·07
Mixture pH 8·0	0·526	4·08
pH 9·0	0·332	4·10
pH 7·5	0·555	4·07
pH 9·5	0·225	4·10

ordinate method was not mandatory and a simpler selection of wavelength values was made; namely, u-range: 410, 420, 430, 440 and 450 mμ; v-range: 460, 470, 480, 490 and 500 mμ; w-range: 520, 530, 540, 550 and 560 mμ. The values of u_a calculated were 0·579 and 0·575, selecting the pH values of the pairs 7·5 and 9·5; and 8·0 and 9·0, respectively. These values and especially their average, 0·572, compare very favourably with the value obtained directly from the experimental data in Table II, namely, 0·572.

J_a was then calculated by equation (15), employing the two pairs of pH values. The values thus obtained, namely 4·06, and 4·07$_6$, and their average, 4·07, are in agreement with the experimental value obtained directly, 4·07.

Since the quotients of differences are involved in all of these calculations, small experimental errors can cause considerable deviations. It is therefore desirable to calculate the values from several sets of curves and then to average the results.

When such an amount of calculation and measurement is involved it would obviously be much simpler to run one single curve at the desired pH value and to obtain the results directly from that curve. The simple indicator equilibrium, however, is treated as an instructive example and the procedure derived may advantageously be applied to the study of cases where overlapping equilibria prevent the direct determination of the complementary colorimetric parameters of one particular form.

With this conformation of the derivation at hand, the complementary colour parameters of the form of thymol blue existing in strongly acidic medium were calculated with the intermediate yellow form considered as the base form. Then the absorption spectra of solutions of thymol blue at pH 1·0 and 2·0, and at 1·5 and 2·5, were obtained. The same wavelengths were utilised as in the above consideration of the intermediate form. The u_a value thus obtained for the two pairs of pH values were 0·137 and 0·137, and these were applied to the calculation of J_a. The values secured were, respectively, 7·54 and 7·41. The average of these two values, 7·47, was then used to calculate the indicator constant using m-values from the curves at pH 1·0, 1·5 and 2·0. The values of $pK_{in,1}$ obtained, namely, 1·55, 1·59 and 1·56, and their average, 1·5$_7$ are in good agreement with the value 1·6 accepted in the literature.[3]

Methyl red presents an interesting case, as it has two acid forms which to the eye are almost the same shade of red. As can be seen from Fig. 2, the absorbance curves of these two forms are rather similar and the differences occur in a wavelength range in which the eye is not especially sensitive. By selecting an appropriate number of absorbance curves to cover the pH region, it is possible to calculate the indicator constant for the transition between the two forms. It should be appreciated that knowledge of these indicator constants is of little or no significance in the usual application of methyl red as an acid-base indicator; however, knowledge of the complementary colour parameters is necessary in order to calculate the exact screening condition for this indicator. These parameters were calculated in the same manner as described above and were then used to secure the values of the indicator constants. The average value of $pK_{in,2}$ (single values 4·88, 5·00 and 4·98) was found to be 4·9$_3$ which is in agreement with the value 4·9 in the literature.[3] The value of $pK_{in,2}$ was found to be 2·3; the same value is recorded in the literature.[4]

When the manuscript of the present paper was in preparation a paper by Reilley and Smith[5] was published. The authors devoted a part of the paper to the determination of indicator constants. Using a somewhat different approach they obtained the constants through a graphical procedure. Incidentally, they also determined the value of $pK_{in,1}$ for methyl red and reported the values 2·3.

Complementary tri-stimulus colorimetry in the study of equilibria

The appropriate plotting of results derived by complementary tri-stimulus colorimetry offers an excellent tool for the study of equilibria involving colorants. If, as with an acid-base indicator, a simple equilibrium is involved, one component disappears and another appears. In such a case a *u—v*, *u—w* or *v—w* plot will yield a straight line. The theoretical background and mathematical derivations have previously been given.[1,2] Such a plot for thymol blue is given in Fig. 3. From point "*a*", denoting the complementary colour point of the indicator form existing in a strongly acidic medium, a straight line passes to point "*i*", corresponding to the intermediate (yellow) form that exists over a wide pH range. With a further increase in pH, the system is represented by a straight line connecting point "*i*" with point "*b*", which corresponds to the form existing in strongly alkaline medium. The calibration of the system lines in pH-units does not result in an equally spaced argument; rather there is "crowding" toward the points "*a*", "*i*" and "*b*". The diagram shown in Fig. 3 can be better appreciated by comparison with the plot shown in Fig. 4.

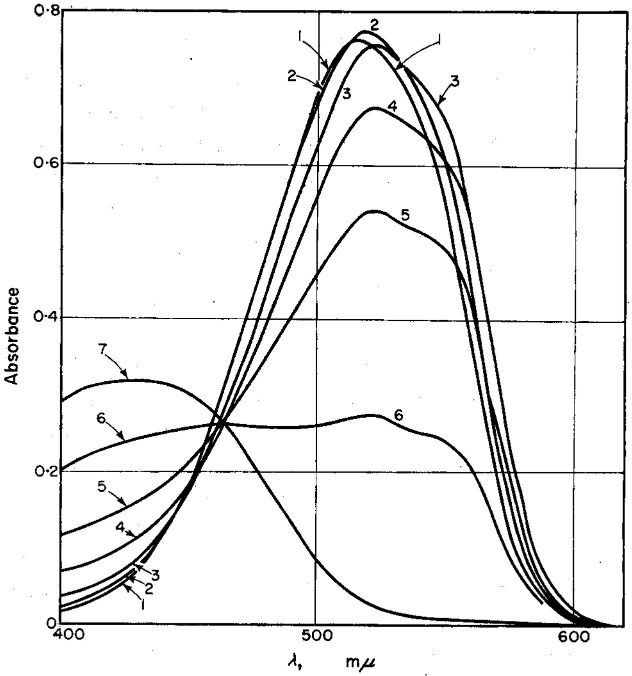

FIG. 2.—Absorbance curves of methyl red at various pH values (1-cm cell).

It is important to appreciate that a pH-Q_r plot (such as in Fig. 4) will not of necessity disclose the occurrence of a multi-step equilibrium. This is illustrated by Fig. 5, which pertains to methyl red. Neither the *u*- nor the *v*-curve reveals that a second equilibrium is operative.

In both curves, the deviations in the region pH 1–4 may be attributed to experimental errors. The *w*-curve, however, shows clearly the presence of a second equilibrium. This can be readily understood by a study of the spectral curves (see Fig. 2); the changes predominate only in the wavelength region selected as the *w*-range. The two steps of the equilibria are immediately apparent from a *u*—*w* plot as shown in Fig. 6. There is an important association between the existence of a straight line in a *u*—*v* plot and the presence of an isobestic point in the absorbance curves. Both are necessary, but insufficient, conditions for a simple equilibrium.

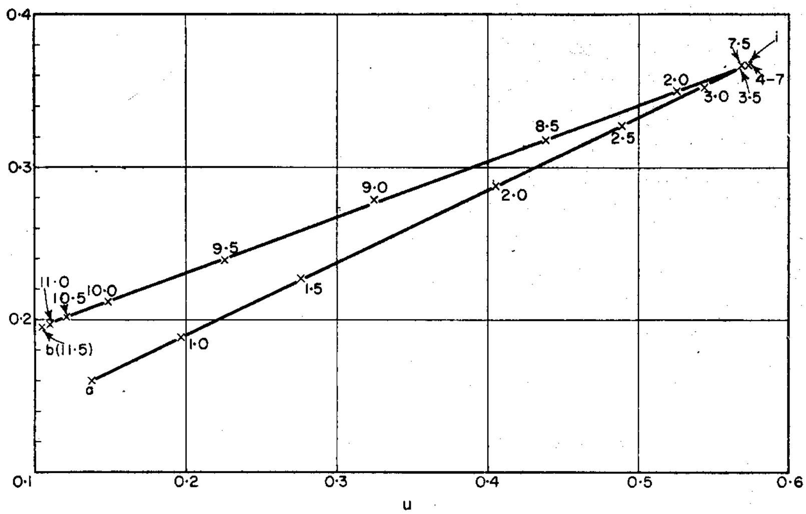

FIG. 3.—*u*–*v* Plot for thymol blue.
Numbers along the lines are the pH values corresponding to the indicated points; *a* represents the acid form, *i* the intermediate (yellow) form, and *b* the base form.

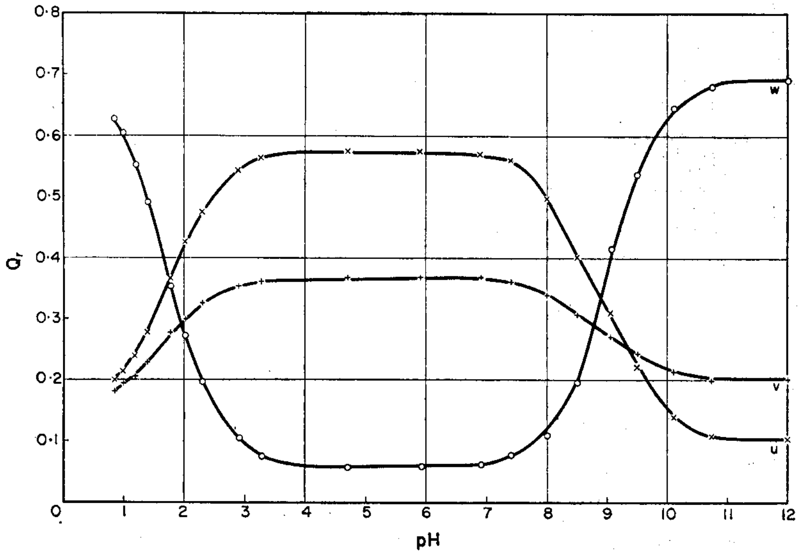

FIG. 4.—Relation of the values of *u*, *v* and *w* to pH for thymol blue.

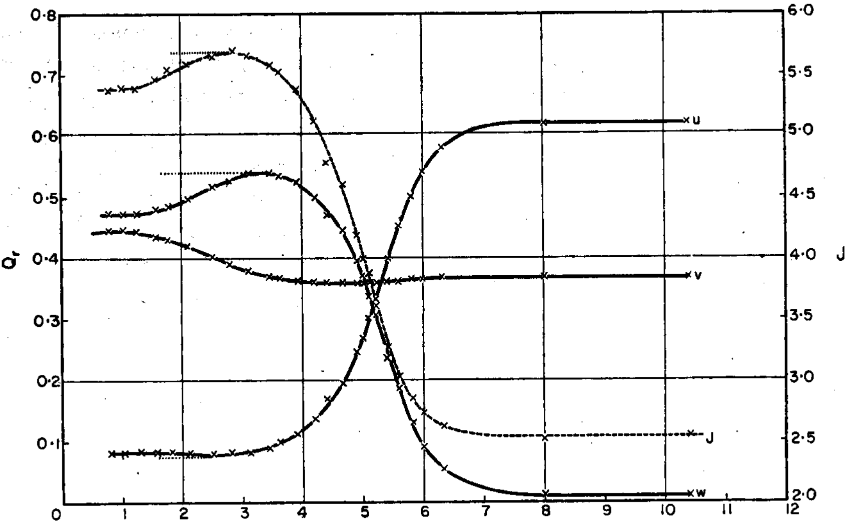

FIG. 5.—Relation of the values of *u*, *v*, *w* and *J* to pH for methyl red.

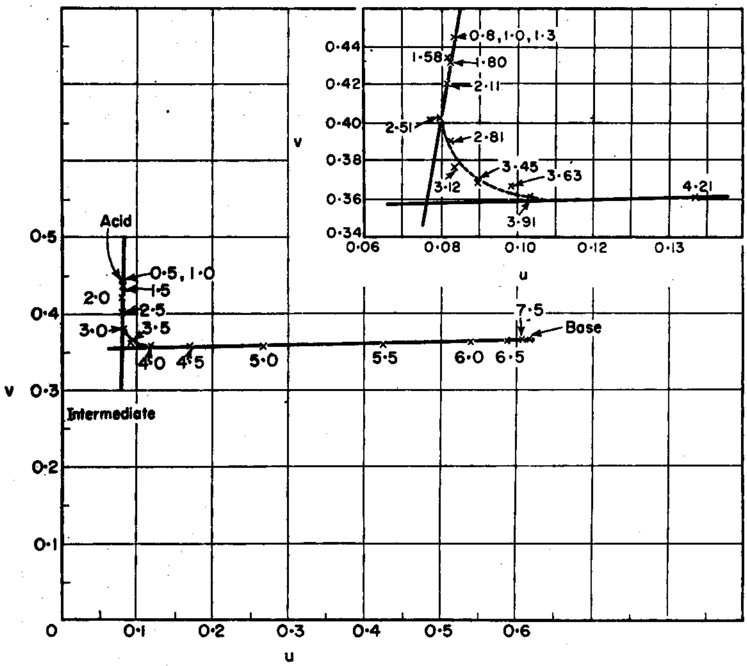

FIG. 6.—*u–v* Plot for methyl red.

Numbers along the lines are the pH values corresponding to the indicated points. The portion of the system in the vicinity of the colour point of the intermediate form is shown enlarged as an insert.

From this point of view, a closer inspection of the system lines around the intermediate form of methyl red does reveal a curvature (see insert in Fig. 6). To date, the present author has been unable to explain this curvature. It may be caused by some impurity which exhibits indicator properties. Hence the value for pK_1 obtained is somewhat uncertain and the problem needs further investigation.

Calculation of screening conditions

The equations derived in this paper may be applied inversely to the calculation of the complementary colour co-ordinates for any indicator colour in the transition interval, when the indicator constant and the complementary colour co-ordinates of the two limiting forms of that particular transition range are known. Then the screening conditions can readily be calculated for any desired pH in the transition interval. For this particular calculation, of course, not any ordinates may be selected; rather, since reference to the eye is maintained, the ordinates must be selected according to the colour theory. The approach can be readily explained in terms of a practical example, namely, the screening of the acid-base indicator methyl orange at pH 4·08. (This particular value was selected because an absorbance curve was available for it, thus permitting comparison of calculated and experimental results). The concentrations of the indicator and of the screening dye (or dyes) in the screened solution can be calculated from the following equation, which was derived in a previous paper:[1]

$$\sum_{i}^{n} (Q_{r,i} - G_r)J_i = 0. \tag{16}$$

In this equation G_r represents the complementary colour co-ordinates of the grey point, that is, the complementary colour point obtained for the illuminant alone with no colorants present. The corresponding values for illuminant C (representing average day-light) are $u = 0{\cdot}310$, $v = 0{\cdot}316$ and $w = 0{\cdot}374$. Equation (16) is actually equivalent to three equations with $r = 1$, 2, and 3 for u, v and w respectively. Since only two unknowns are involved if two screening dyes are employed (the unknowns are the dye concentrations), only two equations need be considered. These two equations may be written explicitly as follows

$$(u_e - 0{\cdot}310)J_e + (u_{bl} - 0{\cdot}310)J_{bl} + (u_v - 0{\cdot}310)J_v = 0, \tag{17}$$

and

$$(v_e - 0{\cdot}316)J_e + (v_{bl} - 0{\cdot}316)J_{bl} + (v_v - 0{\cdot}316)J_v = 0, \tag{18}$$

where the subscripts e, bl and v refer, respectively, to the end-point colour, and the blue and violet screening dyes. These equations can be simplified for further manipulation by introducing the following definitions

$$(u - 0{\cdot}310) = \bar{u}, \tag{19}$$

and

$$(v - 0{\cdot}316) = \bar{v}. \tag{20}$$

This operation represents a shift of the origin of the co-ordinate system from $u = 0$, $v = 0$ to the grey point. Applying this transformation to equations (17) and (18), the following equations are obtained

$$\bar{u}_e J_e + \bar{u}_{bl} J_{bl} + \bar{u}_v J_v = 0, \tag{21}$$

and

$$\bar{v}_e J_e + \bar{v}_{bl} J_{bl} + \bar{v}_v J_v = 0. \tag{22}$$

What has to be found is in essence the ratio of the volumes of the three solutions, namely of the indicator and of the two screening dyes, which must be mixed in order to secure screening at the selected pH. This can be done by introducing the concept "optical millimoles" and "optical molarity". (One could even speak of the "J-ity" of a colorant solution, thus paralleling the molarity.) Then the following equation may be written:

$$ml' \times J' = (J \times ml) \text{ screened solution}, \tag{23}$$

where J' stands for the optical molarity of the stock solution of the three colorants and ml' stands for their volume in millilitres. Equations (21) and (22) can then be written in the following forms:

$$\frac{\bar{u}_e J_e' ml_e'}{ml_e} + \frac{\bar{u}_{bl} J_{bl}' ml_{bl}'}{ml_{bl}} + \frac{\bar{u}_v J_v' ml_v'}{ml_v} = 0, \tag{24}$$

and

$$\frac{\bar{v}_e J_e' ml_e'}{ml_e} + \frac{\bar{v}_{bl} J_{bl}' ml_{bl}'}{ml_{bl}} + \frac{\bar{v}_v' J_v' ml_v'}{ml_v} = 0. \tag{25}$$

Of course the volume of the screened solution is the same for all three components; hence, $ml_e = ml_{bl} = ml_v = ml$. This term, which factors out, vanishes because the resulting product equals zero. Then the final result is

$$\bar{u}_e J_e' ml_e' + \bar{u}_{bl} J_{bl}' ml_{bl}' + \bar{u}_v J_v' ml_v' = 0, \tag{26}$$

and

$$\bar{v}_e J_e' ml_e' + \bar{v}_{bl} J_{bl}' ml_{bl}' + \bar{v}_v J_v' ml_v' = 0. \tag{27}$$

In these equations $\bar{u}_e'\bar{v}_e$ and J_e' can be calculated from the corresponding data for the limiting forms of the acid-base indicator, and $\bar{u}_{bl}$, $\bar{v}_{bl}$, $\bar{u}_v$, $\bar{v}_v$, J_{bl}' and J_v' are known from the absorbance curves of the stock solution of the screening dyes.

It is now possible to make ml_e' unity and to solve for the two unknowns ml_{bl}' and ml_v'. This then gives the number of millilitres of each of the stock solutions of the screening dyes which must be mixed with 1 ml of the indicator stock solution in order that the mixture will exhibit grey at the selected pH value.

Solution of the equations is best accomplished by employing determinants and applying Cramer's rule. The result is

$$ml_e' \colon ml_{bl}' \colon ml_v' = 1 \colon \frac{J_e'}{J_{bl}'} A \colon \frac{J_e'}{J_v'} B, \tag{28}$$

where

$$A = \frac{\begin{vmatrix} \bar{u}_v & \bar{u}_e \\ \bar{v}_v & \bar{v}_e \end{vmatrix}}{\begin{vmatrix} \bar{u}_{bl} & \bar{u}_v \\ \bar{v}_{bl} & v_v \end{vmatrix}}, \tag{29}$$

and

$$B = \frac{\begin{vmatrix} \bar{u}_e & \bar{u}_v \\ \bar{v}_e & \bar{v}_v \end{vmatrix}}{\begin{vmatrix} \bar{u}_{bl} & \bar{u}_v \\ \bar{v}_{bl} & \bar{v}_v \end{vmatrix}}. \tag{30}$$

By applying equation (3) to methyl orange at pH 4·08, the q value can be calculated and is found to be 0·193. Then by applying either equation (4) or (6), and replacing the E values by the J values according to equation (8), the complementary colour co-ordinates $\bar{u}$ and $\bar{v}$ for the end point colour are obtained. Finally J for the end-point colour, that is at pH 4·08, is obtained by application of equation (12). It can be proved very simply that in the latter calculation the Q_r values can be taken instead of the $\overline{Q_r}$ values.

These values and the corresponding values for the two screening dyes are collected in Table III, which also contains the results obtained from the spectral curve for methyl orange at pH 4·08. Application of equations (28), (29) and (30) established that the volumes of the violet and blue screening dye solutions to be added to one millilitre of indicator stock solution were, respectively, 0·509 and 0·888 ml. The three solutions were then mixed in these indicated proportions and several drops of the resulting solution were added to a dilute hydrochloric acid solution. An aliquot of this solution was then titrated with sodium hydroxide solution by three different persons in average daylight to the grey point. The pH values of the titrated solutions were measured and were found to be 4·00, 4·02 and 4·06. The agreement is excellent when it is recognised that none of the observers possesses the hypothetical "average" eye and that the illuminant did not exactly correspond to standard illuminant *C*. Fig. 7 shows the absorbance curve for the screened indicator at appropriate dilution and brought to exactly pH 4·08. The $\bar{u}$ and $\bar{v}$ values of that curve are 0·313 and 0·314, which within experimental error corresponds to the actual co-ordinates of the grey point, that is, 0·310 and 0·316, respectively.

TABLE III.—COMPLEMENTARY COLORIMETRIC PARAMETERS FOR CALCULATING THE SCREENING CONDITIONS OF METHYL ORANGE

	$\bar{u}$	$\bar{v}$	J
Indicator acid form	−0·177	0·055	28·29
base form	−0·173	−0·214	21·83
pH 4·00 calculated	−0·174	−0·150	23·08
pH 4·08 experimental	−0·173	−0·152	23·26
Screening dye Blue CI 671	0·274	0·081	16·61
Violet CI 697	0·071	0·246	24·35

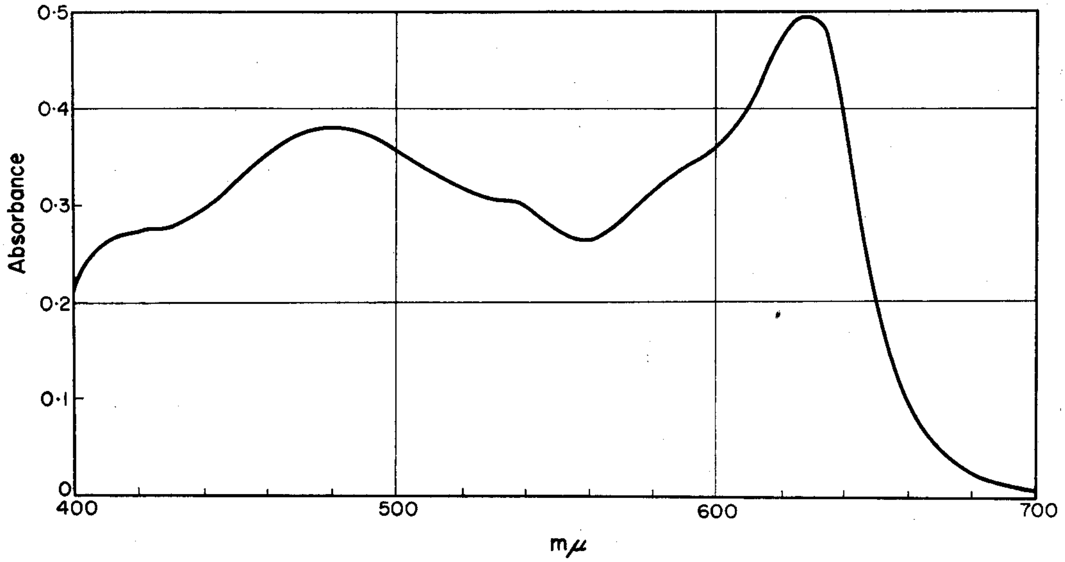

FIG. 7.—Absorbance curve of the screened methyl orange indicator at pH 4·08 (5-cm cell).

When a similar approach was applied to the screening of tetrabromophenolphthalein good agreement was also obtained. In this case, however, it proved to be advisable to use a rather low concentration of the indicator in the solution to be actually titrated and to observe the end-point colour change through a short light path. The screened indicator mixture exhibits dichromatism to a higher degree than the pure indicator. This observation was also made with some other systems, and further studies are being made of this phenomenon. Probably such difficulties can be overcome by appropriate selection of the screening dyes.

EXPERIMENTAL

All reagents used were of analytical grade except the screening dyes which were applied as obtained from the manufacturer. The absorbance curves of the indicators were obtained in the following manner: A stock solution of the indicator was prepared in either water or alcohol, as appropriate. Then a known volume of this stock solution was transferred to a volumetric flask and diluted to the mark with $0{\cdot}1N$ hydrochloric acid. A second identical aliquot of the stock solution was transferred to a second volumetric flask (of the same volume as the first) and diluted to the mark with $0{\cdot}1N$ sodium hydroxide. Some of the acidic indicator solution was transferred to a beaker and titrated with the basic solution. The pH values were measured with a Beckman pH meter and portions of the solution having the appropriate pH values were transferred to cuvettes and their absorbance curves measured by use of a Cary model 14 recording spectrophotometer. Absorbance and pH measurements were made at room temperature 25 ± 2°.

Acknowledgements—Dr. A. J. Barnard Jr., Phillipsburg, N.J., is thanked for helpful criticism of the manuscript. Mr. A. L. Chason and Mr. A. J. Shingler of The Coca-Cola Company, Atlanta, Ga., are thanked for arranging for use of the recording spectrophotometer of that company. The work was supported by a grant of the National Science Foundation.

Zusammenfassung—Es wird gezeigt, dass die Indikatorkonstanten von Säure-Basenindikatoren mittels komplementärer Tristimulusdaten errechnet werden können. Es wird hingewiesen, dass diese Art von Berechnungen auch auf ähnliche Gleichgewichte ausgedehnt werden kann. Aus den komplementären Tristimulusparametern für den Indikator und für die zuzumischenden, inerten Farbstoffe, sowie der Indikatorkonstante kann die Zusammensetzung einer Indikatormischung berechnet werden, die bei einem bestimmten pH-Wert ein neutrales Grau zeigt. ("Gescreenter" Indikator).

Résumé—L'auteur montre que les constantes des indicateurs acide-base peuvent être calculées à partir des résultats des tristimuli. Il fait remarquer que cette méthode est applicable à l'étude et à l'évaluation d'équilibres semblables. A partir des résultats des trismuli pour un indicateur acide-base et pour un colorant (ou des colorants) "protecteur" et de la constante calculée de l'indicateur, la composition d'une solution stable d'indicateur "protégé" de façon satisfaisante peut être calculée. Des exemples sont donnés et des valeurs dérivées sont comparées avec les résultats expérimentaux.

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SELECTION OF COMPLEXING AGENTS FOR COMPLEXOMETRIC TITRATIONS*

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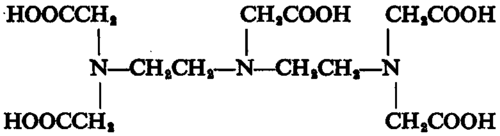
Summary—It is shown how conditional (*i.e.*, apparent) constants can be used to choose the most suitable complexing agent for the titration of a metal in the presence of other metals. The titration of barium is considered as an example. This titration can be performed with satisfactory accuracy with DTPA or EGTA, employing indirect end-point detection. Curves plotting the theoretical titration errors of the titrations are presented.

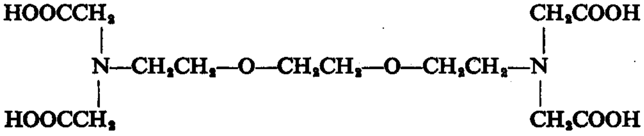
Calcium can be determined in the presence of magnesium with EGTA, using Zincon and zinc-EGTA for indirect end-point detection. The theoretical titration error has been evaluated for titrations under various experimental conditions.

ETHYLENEDIAMINETETRA-ACETIC acid (EDTA) holds a special position as a titrant in complexometric titrations, but frequently better results can be obtained in titrations if another polyamino-polycarboxylic acid is substituted for it. In recent years the applicability of several polyamino-polycarboxylic acids as complex-forming titrants has been studied, and in this paper two of these acids, diethylenetriaminepenta-acetic acid (DTPA), and ethyleneglycol-bis-(aminoethylether)tetra-acetic acid (EGTA), will be compared with ethylenediaminetetra-acetic acid to determine whether they are more suitable titrants than EDTA itself.



$$(HOOCCH_2)_2N-CH_2CH_2-N(CH_2COOH)-CH_2CH_2-N(CH_2COOH)_2$$

Diethylenetriaminepenta-acetic acid
(DTPA)



$$(HOOCCH_2)_2N-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-N(CH_2COOH)_2$$

Ethyleneglycol-bis-(aminoethylether)tetra-acetic acid
(EGTA)

FIG. 1.

The structures of the two new acids are shown in Fig. 1. The complexing properties of these acids can be compared with those of EDTA by choosing a suitable reference metal.

The comparison can be made most simply by plotting the values of the *conditional*

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* A paper read at the 10:e Nordiska Kemistmötet, Stockholm, 1959.

*constants** of the complexes formed by this metal with the three acids as functions of pH. The conditional constant of a 1:1 complex MY, formed by the metal M and the complexing agent H_nY, is computed from the equation:

$$K_{M'Y'} = [MY]/([M'][Y']) = K_{MY}/(\alpha_M \alpha_Y), \tag{1}$$

where K_{MY} is the stability constant of the complex at the ionic strength in question and α_M and α_Y are so-called side-reaction coefficients[2] defined by

$$\alpha_M = [M']/[M], \tag{2}$$

$$\alpha_Y = [Y']/[Y]. \tag{3}$$

[M′] denotes the concentration of the metal ion and [Y′] the concentration of the complexing agent (ligand) that has *not* reacted to form the complex MY, irrespective of the form in which each exists in the solution. In an ammoniacal solution, for example, the metal ion may form several complexes with ammonia, and then

$$[M'] = [M] + [M(NH_3)] + [M(NH_3)_2] + .. + [M(NH_3)_p]. \tag{4}$$

Similarly, if no interfering cations other than the hydrogen ion are present, we may write

$$[Y'] = [Y] + [HY] + [H_2Y] + .. + [H_nY]. \tag{5}$$

The numerical values of the side-reaction coefficients are calculated with the aid of the equations:

$$\alpha_{M(L)} = 1 + \sum_{p=1}^{p} [L]^p K^M_{ML_p}; \qquad K^M_{ML_p} = [ML_p]/([M][L]^p), \tag{6}$$

and

$$\alpha_{Y(N)} = 1 + \sum_{q=1}^{q} [N]^q K^Y_{N_qY}; \qquad K^Y_{N_qY} = [N_qY]/([N]^q[Y]), \tag{7}$$

in which L denotes an interfering ligand (an anion, which may be the hydroxyl ion, or a molecule) and N denotes an interfering cation (also the hydrogen ion).

If N in equation (7) represents the hydrogen ion, $K^Y_{N_qY}$ is the over-all proton stability constant defined by the equation

$$K^Y_{N_qY} = K^Y_{H_nY} = [H_nY]/([H]^n[Y]). \tag{8}$$

For the comparison of the properties of the complexing agents we present the values of the conditional constants of the barium complexes of the acids. Because the barium ion does not form complexes with the hydroxyl ion or ammonia, α_{Ba} is equal to unity and the value of the conditional constant varies inversely as $\alpha_{Y(H)}$. The variation of the conditional constants of the different barium complexes is shown by the curves in Fig. 2.

The possible formation of binuclear barium complexes of DTPA,[5] which would cause the value of α_{Ba} to deviate from unity, has not been taken into account when computing the values of the conditional constant of the barium-DTPA complex, but this formation cannot be expected to have any appreciable influence on the calculated curve.

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* The term "conditional constant", which corresponds to "apparent constant" employed by Schwarzenbach,[1] was introduced by Kolthoff and Ringbom.[2,3] Reilley[4] has used the name "effective constant" for the same purpose.

It will be seen from Fig. 2 that DTPA and EGTA are the best complexing agents for the titration of barium at pH 10. For direct end-point detection the indicator Metalphthalein[6] could be employed, but owing to the tendency of the indicator to form coloured acid and binuclear complexes, its use requires a very accurate adjustment of the pH of the solution (to pH $\simeq$ 11·5). Other means of end-point detection have been proposed. Thus Schwarzenbach[1] has suggested the use of Eriochrome Black T, together with the magnesium or zinc complex of the complexing agent, in the titration of barium with EDTA. The sharpness of the colour change is not, however, quite satisfactory in this case, and therefore it is of interest to determine whether a better end-point detection can be achieved with DTPA or EGTA.

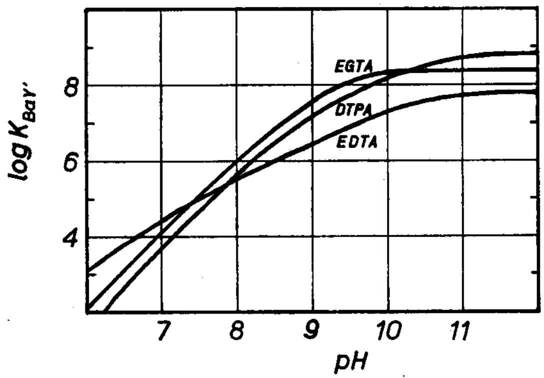

FIG. 2.—Conditional constants of barium complexes as functions of pH.

The Titration of Barium with Indirect End-point Detection

The theoretical treatment of a titration with indirect end-point detection requires a knowledge of the equilibrium conditions of the reactions:

$$M_I + M_{II}Y \rightleftharpoons M_IY + M_{II} \tag{9}$$

$$M_{II} + I \rightleftharpoons M_{II}I. \tag{10}$$

M_I is the metal ion to be determined, Y the complexing agent, M_{II} an added auxiliary metal ion, and I an indicator that changes colour when it reacts with the latter metal ion. When Eriochrome Black T is employed as indicator, the most suitable auxiliary metal ion is magnesium or zinc.

The values of the stability constants of the barium, magnesium and zinc complexes of the three complexing agents under consideration are collected in Table I.

TABLE I.—VALUES OF THE STABILITY CONSTANTS OF THE BARIUM, MAGNESIUM AND ZINC COMPLEXES OF DTPA, EGTA AND EDTA.

	$\log K_{MgY} - \log K_{BaY}$	$\log K_{ZnY} - \log K_{BaY}$
DTPA	$9·3 - 8·8 = \underline{\underline{0·5}}$	$18·0 - 8·8 = 9·2$
EDTA	$8·7 - 7·8 = 0·9$	$16·5 - 7·8 = 8·7$
EGTA	$5·4 - 8·4 = -3·0$	$12·8 - 8·4 = \underline{\underline{4·4}}$

A. *Titration of barium in the presence of the magnesium complex of the complexing agent*

In order that Eriochrome Black T and the magnesium complex of the complexing agent can be employed to indicate the end-point of the titration of barium with another complexing agent, with a greater accuracy than with EDTA as titrant, the difference between the stability constants of the magnesium and barium complexes must be smaller for the former complexing agent than for EDTA. The difference

$$\Delta \log K^{\mathrm{Mg,Ba}} = \log K_{\mathrm{MgY}} - \log K_{\mathrm{BaY}} \qquad (11)$$

is seen to be the smallest for EGTA ($\Delta \log K^{\mathrm{Mg,Ba}}_{\mathrm{EGTA}} = -3{\cdot}0$), but since the stability constant of the magnesium complex must exceed the value 10^7 before the end-point can be detected visually with sufficient accuracy, DTPA is more suitable for the determination of barium. This has been shown to be the case previously in the analysis of small amounts of barium and, indirectly, of small amounts of sulphate.[7]

The theoretical titration error in such a complexometric titration is given by

$$\text{Titration error} = ([\mathrm{Y}'] - [\mathrm{M_I}'] - [\mathrm{M_{II}}'])/[\mathrm{M_I Y}]. \qquad (12)$$

When conditional constants are introduced into this equation, we obtain

$$\begin{aligned}\text{Titration error} = {} & [\mathrm{M_{II}Y}]/([\mathrm{M_I Y}][\mathrm{M_{II}}']\, K_{\mathrm{M_{II}'Y'}}) \\ & - [\mathrm{M_{II}}']\, K_{\mathrm{M_I'Y'}}/([\mathrm{M_{II}Y}]\, K_{\mathrm{M_{II}'Y'}}) - [\mathrm{M_{II}}']/[\mathrm{M_I Y}]. \qquad (13)\end{aligned}$$

The theoretical titration error in the titration of barium ($= \mathrm{M_I}$) with DTPA, in the presence of the magnesium-DTPA ($= \mathrm{M_{II}Y}$) complex, is plotted as a function of the concentration of the latter in Fig. 3. At pH 10 Eriochrome Black T turns blue when $[\mathrm{Mg}] \leq 10^{-5{\cdot}9}$ (pMg $\geq 5{\cdot}9$).

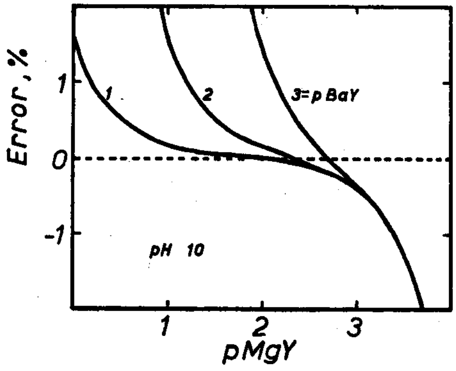

FIG. 3.—Theoretical titration error in the simultaneous titration of barium and magnesium ions with DTPA as a function of the concentration of added magnesium-DTPA complex. pH 10. $\mathrm{pMg_{end\text{-}p.}} = 5{\cdot}9$. Indicator : Eriochrome Black T.

From the Figure it is seen that good results can be expected when the magnesium complex is added to a barium salt solution of unknown concentration until its concentration is about $10^{-3}M$. Titration errors[7] found experimentally conform fairly well with the curves shown in Fig. 3.

B. *Titration of barium in the presence of the zinc complex of the complexing agent*

When the zinc complex and Eriochrome Black T are employed for indirect end-point detection in the titration of barium, the difference between the stability constants of the zinc and barium complexes of the new titrant must be smaller than the difference for the corresponding complexes of EDTA. This difference is seen to be smallest for EGTA (Table I), and hence this complexing agent is more suitable than EDTA for the titration of barium.

Eriochrome Black T can be employed, together with the zinc complex of the complexing agent, as an indicator for the indirect end-point detection in the titration of barium, if the conditional constant of the zinc complex is of the same order of magnitude as that of the barium complex. Only when this is the case can the indicator react with the zinc ions that are liberated by reaction (9), and a titration is then possible. The conditional constant of the zinc complex can be diminished by adding another complexing agent that reacts only with the zinc ion. Ammonia is a suitable reagent for this purpose. Values of $\alpha_{Zn(NH_3)}$ computed from equation (6), and the values of the conditional constant ($K_{Zn'I'}$) of the zinc-Eriochrome Black T complex ($\log K_{ZnI} = 12{\cdot}9$) at various ammonia concentrations, are given in Table II. The conditional constant of the zinc-indicator complex is computed from

$$K_{Zn'I'} = K_{ZnI}/(\alpha_{Zn(NH_3)}\alpha_{I(H)}). \tag{14}$$

TABLE II.—$\alpha_{Zn(NH_3)}$ AND $K_{Zn'I'}$ AS FUNCTIONS OF THE AMMONIA CONCENTRATION AT pH 10.

$-\log [NH_3]$	0	0·5	1·0	1·5	2·0
$\log \alpha_{Zn(NH_3)}$	9·0	7·0	5·0	3·1	1·5
$\log K_{Zn'I'}$	2·3	4·3	6·3	8·2	9·8

The calculations have been based on the stability constants of the zinc ammine complexes given in Bjerrum, Schwarzenbach and Sillèn's[8] compilation.

From Table I it can be seen that the conditional constant for the zinc-EGTA complex should be lowered by 4·4 logarithmic units in order that EGTA's barium- and zinc complexes shall be equally strong, and the corresponding lowering on titration with EDTA ought to be 8·7 units. Table II gives information on the ammonia concentration which the solution should contain in order that the necessary lowering of the conditional constant of the zinc complex shall be attained. In the former case about 0·1*M* ammonia is sufficient, in contrast to the latter, which requires about 1*M* concentration.

At a lower ammonia concentration the value of $\alpha_{Zn(NH_3)}$ will be lower, and the conditional constant of the zinc-indicator complex higher in value. When the conditional constant of the zinc-indicator complex is too low, as in the titration with EDTA ($\log K_{Zn'I'} = 2{\cdot}3$), a visual end-point detection is not possible. This difficulty can, in some degree, be overcome if the zinc-indicator complex reacts with ammonia to form a so-called heterobiligand zinc-ammine-indicator complex. Reilley and Schmid[9] have determined the stability constant of the mixed zinc-ammine complex of the indicator Eriochrome Blue Black R and obtained the value $K^{NH_3}_{NH_3ZnI} = 10^{3{\cdot}9}$

The formation of such a complex increases the conditional constant of the zinc-indicator complex to the value given by

$$K_{Zn'I'(ZnI)'} = \alpha_{ZnI(NH_3)} K_{ZnI}/(\alpha_{Zn(NH_3)}\alpha_{I(H)}) \qquad (15)$$

where

$$\alpha_{ZnI(NH_3)} = 1 + [NH_3]\, K^{NH_3}_{NH_3ZnI}\,; \quad K^{NH_3}_{NH_3ZnI} = \frac{[NH_3ZnI]}{[ZnI][NH_3]}\,. \qquad (16)$$

The curves in Fig. 4 plot the theoretical titration error in the titration of barium with EGTA, in the presence of zinc-EGTA, at different ammonia concentrations. The errors have been computed from equation (13).

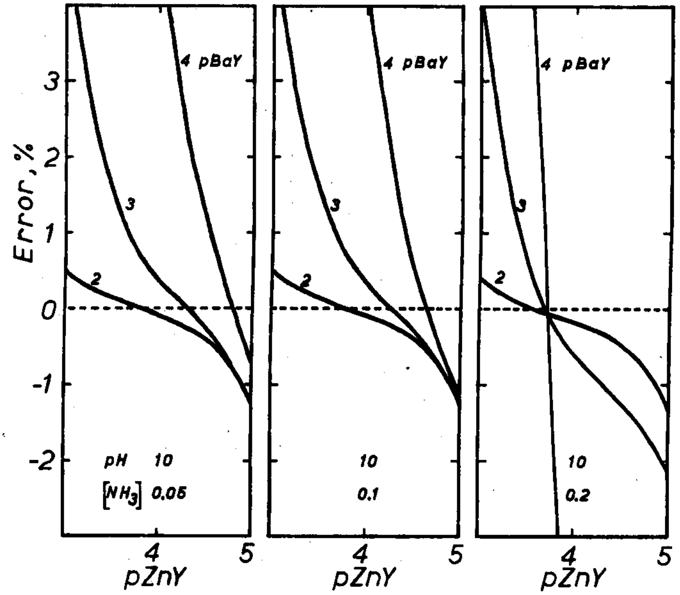

FIG. 4.—Theoretical titration error in the titration of barium with EGTA as a function of the concentration of added zinc-EGTA complex and of the ammonia concentration at pH 10. Indicator: Eriochrome Black T.

Experimentally determined titration errors are in satisfactory agreement with the theoretical errors plotted in Fig. 4, except at high ammonia concentrations, where positive errors are found. This is evidently because of the formation of the zinc-ammine-indicator complex.

The titration employing zinc and EGTA is more accurate than that in which magnesium and DTPA are used.

The titrations of barium with EGTA were performed as follows:

To 10 ml of an approximately 0·01*M* barium chloride solution were added 5 ml of buffer solution (2*M* in ammonia and 0·4*M* in ammonium chloride; pH 10), 5 ml of 0·002*M* zinc-EGTA solution, 0·5 ml of 0·1% alcoholic Eriochrome Black T solution, and the resulting solution was diluted to 80 ml with distilled water. The titration was carried out with 0·0233*M* disodium ethyleneglycol-bis-(aminoethylether)tetra-acetate solution.

The results of a number of titrations conducted in the presence of different ammonia and zinc-complex concentrations are collected in Table III. The colour change from red to blue was relatively sharp when the ammonia concentration was suitable (0·05–0·1*M*).

TABLE III.—TITRATION OF BARIUM WITH EGTA IN THE PRESENCE OF ZINC-EGTA AND AMMONIA. pH 10.

pZnY	$[NH_3]$	Barium taken, *mmole*	Barium found, *mmole*	Error, %
3·4	0·05	0·0999	0·1004	+0·4
3·7			0·1002	+0·2
4·0			0·1000	+0·1
4·7			0·0962	−3·7[a]
4·0	0·1		0·1004	+0·4
4·0	0·2		0·1030	+3·0[b]
4·0	0·25		0·1055	+5·5[b]

[a] pZnY too high
[b] $[NH_3]$ too high

Titration of Calcium in the Presence of Magnesium

A condition that must be fulfilled before a metal ion M_I can be titrated in the presence of a second metal ion M_{II} is that the difference between the logarithmic conditional constants of the complexes formed by the two metals

$$\Delta \log K^{M_I'M_{II}'} = \log K_{M_I'Y'} - \log K_{M_{II}'Y'} \tag{17}$$

is sufficiently large (at least four logarithmic units). In addition, as previously mentioned, the conditional constant $K_{M_I'Y'}$ of the complex of the first metal must be larger than 10^7 before a visual titration of the metal ion M_I can succeed.

A titration of calcium in the presence of magnesium is, therefore, not possible with EDTA or DTPA ($\Delta \log K^{Ca,Mg}_{EDTA} = 2{\cdot}0$; $\Delta \log K^{Ca,Mg}_{DTPA} = 1{\cdot}3$), but can be carried out with EGTA because the difference between the logarithmic conditional constants of the EGTA complexes of the two metals is 5·6. A method, based on the use of this complexing agent and an indirect end-point detection, has been proposed by Ringbom, Pensar and Wänninen[10] and later by Sadek, Schmid and Reilley.[11]

The reaction $M_{II} + Y \rightleftharpoons M_{II}Y$ interferes in the determination of M_I and the degree of the interference is determined by the stability constant of the complex $M_{II}Y$ and the concentration of the metal ion M_{II}. Ringbom[2,3] has shown that this reaction can be considered a normal side reaction of the complexing agent which requires the introduction of the side reaction coefficient

$$\alpha_{Y(M_{II})} = ([Y] + [M_{II}Y])/[Y] = 1 + [M_{II}]\, K_{M_{II}Y} \tag{18}$$

into the expression for the over-all coefficient α_Y, which then becomes

$$\alpha_Y = \alpha_{Y(H)} + \alpha_{Y(M_{II})} - 1 \simeq \alpha_{Y(H)} + \alpha_{Y(M_{II})}. \tag{19}$$

If the term $\alpha_{Y(M_{II})}$ is the dominating one in (19), and further, if $[M_{II}]\, K_{M_{II}Y} > 1$, the conditional constant of M_IY may, when $\alpha_{M_I} = 1$, be written

$$\log K_{M_IY'} = \Delta \log K^{M_IM_{II}} + pM_{II}. \tag{20}$$

This equation can be used to evaluate the conditional constant of the calcium complex of EGTA in the presence of magnesium.[10] Since $\log K_{\text{Ca-EGTA}} = 11{\cdot}0$ and $\log K_{\text{Mg-EGTA}} = 5{\cdot}4$,

$$\log K_{\text{CaY}'} = 5{\cdot}6 + \text{pMg}. \tag{21}$$

In the titration, the metal indicator Zincon (2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene) and zinc-EGTA can be employed for indirect end-point detection. The stability constant of the zinc-Zincon complex has been evaluated previously.[10]

Because the determination of calcium in the presence of magnesium is an analysis frequently encountered, an estimate of the accuracy attainable in the titration is of particular interest. The theoretical titration error can be computed with the aid of equation (13). The results of such calculations are shown in Fig. 5.

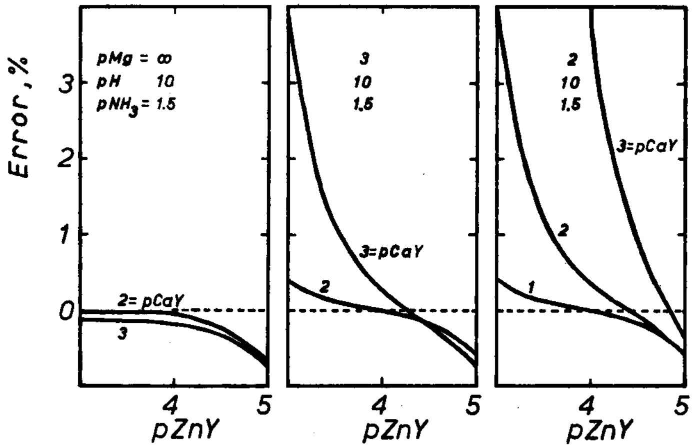

FIG. 5.—Theoretical titration error in the titration of calcium with EGTA at pH 10 in the presence of different concentrations of magnesium ion and zinc-EGTA in solutions containing Zincon and ammonia (0·03*M*). The colour change takes place when pZn′ = 5·9.[10]

It will be seen from Fig. 5 that the titration error is very low, as long as the concentration of the zinc-EGTA complex does not exceed $10^{-4}M$ and the magnesium ion concentration does not exceed that of the calcium ion.

Acknowledgement—I am indebted to Professor Anders Ringbom for stimulating discussions and comments relating to the manuscript.

Zusammenfassung—Es wird gezeigt, wie man die effektiven (scheinbaren) Stabilitätskonstanten heranziehen kann um das bestgeeignete Komplexbildungsreagen für eine Titration eines Metalles in Gegenwart anderer Metalle zu finden. Die Bestimmung von Barium wird als Beispiel herangezogen. Diese Bestimmung kann mit befriedigender Genauigkeit durchgeführt werden, indem man Diäthylentriaminpentaessigsäure (DTPE) und Äthylenglykol-bis-(aminoäthyläther)-tetraessigsäure (ÄGTE) heranzieht und indirekte Endpunktsanzeige verwendet. Titrationskurven werden gezeigt und der Titrationsfehler berechnet. Calcium kann in Gegenwart von Magnesium mit ÄGTE bestimmt werden wobei Zincon-Zink ÄGTE als Indicatorsystem verwendet wird. Der theoretische Titrationsfehler unter verschiedenen Titrationsbedingungen wurde berechnet.

Résumé—L'auteur montre comment les constantes conditionnelles (c'est-à-dire apparentes) peuvent être utilisées pour choisir l'agent complexant le plus convenable pour le titrage d'un métal en présence d'autres métaux. Le titrage du baryum est pris comme exemple. Il peut être réalisé avec une précision satisfaisante par l'acide diéthylènetriaminepentacétique (DTPA) et par l'acide éthylèneglycol-bis-(aminoéthyléther) tétracétique (EGTA) en utilisant une détection indirecte du point équivalent. Des courbes montrant les erreurs théoriques de titrage ont été tracées. Le calcium peut être dosé en présence de magnésium par l'EGTA en utilisant le zincon et le complexe zinc-EGTA pour déceler indirectement le point équivalent. L'erreur de titrage théorique a été évaluée pour des titrages dans différentes conditions expérimentales.

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Talanta, 1961, Vol. 8, p. 364. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

Reported explosion in the periodic acid Liquid Fire reaction

SIR:

I have read the report, by Mr. J. Thomson, of an explosion due to the use of the Smith and Diehl Periodic Acid Liquid Fire reaction. Like all reactions employing perchloric acid, it would appear that users will take particular pleasure in publicising this—if possible in an hysterical tone of expected explosions. This has been the curse of the promotion of perchloric acid reactions—the aim seems to be to give as big a black eye as possible when a perchloric acid reaction gets out of hand. It makes no difference if such reported explosions are obviously the result of faulty techniques.

The Periodic Acid Liquid Fire Reaction is intended for use in the wet oxidation of organic compositions which are essentially cellulose, protein, sugar and polyhydric alcohols, plastics (excluding polyethylene) or coal. I do not know whether the sample used in this violent reaction reported by Mr. Thomson fell into this category or not. But one thing is as clear as crystal, that the published directions call for the use of 1·5 g of periodic acid per gram of material to be oxidised. Mr.Thomson used a 5-g sample, and added only 3 g of periodic acid, whereas 7·5 g are specified. The principal use of periodic acid is to break down the organic material before the reaction of perchloric acid to complete the oxidation. Obviously if one has insufficient periodic acid present the reaction will not be normal.

Then, too, the reaction is easily stopped if it does not show normal features. All you need to do is to pour 25–30 ml of water down the condenser into the reaction mixture, and no violence is then possible. The exothermic reaction building up is then immediately quenched. Mr. Thomson had plenty of time to do this, as his manipulations prove. This would have enabled him to cogitate at his leisure on what fault there was to be found in his experimental approach, and to adjust reagent amounts as required.

The writer has utilised this reaction type before audiences many times without any protection for the experimenter or for the audience. And no violence was predicted or realised.

Since 1920, perchloric acid has been a name to stampede 99 per cent of the world's chemists. The sale in 1920 was a few hundred pounds annually, world wide. To-day, perchloric acid is utilised in control laboratories in the U.S.A. to the extent of two million pounds annually. The number of routine analytical determinations in the control laboratories of the iron and steel, leather, and agricultural control procedure laboratories amounts to many millions of individual determinations annually. This is in spite of a dozen or more perchlorate explosions that have been reported in the chemical literature. But this reagent continues to increase in consumption. Now that the solid fuel rocket programme is to use 100,000 tons of ammonium perchlorate in 1961 (*Chem. Eng. News*), the popularity of perchlorate oxygen carriers will further enhance the field of perchlorate technology, until even the common textbooks of chemistry will begin to teach the basic principles involved.

It was not good practice to report this mishap without first contacting either of the two authors of the published procedure in question. If Mr. Thomson will be so kind as to send me a sample of the pigment involved in his explosion, I will attempt its wet oxidation in my own laboratory and report the proper procedure to employ. And I am sure that I will not fail to find a suitable reaction mixture.

Very truly yours,

G. FREDERICK SMITH
(Professor of Chemistry, Emeritus.)

William Albert Noyes Laboratory
Department of Chemistry and Chemical Engineering
University of Illinois, Urbana, Illinois, U.S.A.
16 *February* 1961

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BOOK REVIEWS

The Use of Organic Reagents in Inorganic Analysis. A. I. Busev and N. G. Polianskii. Translated by J. T. Greaves. Pp. 76. Pergamon Press Ltd., 1960, 21s.

This little book is an English translation of a Russian review article which, apart from a few general references, covers papers published during the years 1953 to 1955 inclusive. The use of organic reagents in chromatography and many applications of complexans in analysis are not included.

There are two chapters in the book; the first rightly deals with general problems in the use and behaviour of organic reagents. The second outlines very briefly what the authors regard as the more important methods of determining the elements using organic reagents.

While the largely uncritical and disjointed presentation of the material is regrettable, there appear to be few mistakes of a technical nature and a good point is the adherence to chemical names rather than the sometimes all too prevalent reliance on trivial names for complicated organic molecules.

In view of the short period of time covered and its limitations in size and scope, the book can hardly be regarded as a major work in this field. It is nevertheless a useful contribution to the literature on organic reagents and it provides English-speaking readers with information (albeit somewhat sketchily and out of date) on developments and trends in this branch of analysis in the Soviet Union.

S. J. Lyle

Chemical Instrumentation. A systematic approach to instrumental analysis. Howard A. Strobel. Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1960. pp. 653. $9.75.

The author mentions in his preface, "this text has grown out of the teaching of two one-semester advanced courses in instrumental analysis, one emphasizing optical methods, the other emphasizing electric techniques." After two excellent introductory chapters on the "Science of Instrumentation" and "Errors of Measurement," there follows seven chapters on "Opticometric Methods" and eight chapters on "Electrometric Methods." In the appendix are outlined twenty-four well chosen experiments designed to illustrate the application of the instruments and techniques common to the modern analytical laboratory.

This book is a refreshing departure from the usual loosely organised texts on this subject in that it treats instrumentation as a science in itself built on the foundations of physics, physical chemistry, and engineering. Accordingly, background chapters on the interaction of electromagnetic radiation and matter, physical optics, electrical and electrochemical theory, and electronics are included. These are generally very well written and amply illustrated with well-conceived figures.

In the chapter on the interaction of electromagnetic radiation and matter, the reviewer is gratified to see a short section devoted to optical dispersion, a subject which unfortunately is usually entirely neglected in other books on instrumentation. However, one feels the rest of this chapter is too brief and not up to the high standard of quality set by the remainder of the book.

One small error was noted on page 41 in the legend of Fig. 3–5 which gives the impression that radiative transitions from excited electronic states can occur in 10^{-14} to 10^{-7} sec. A figure of 10^{-9} sec. would be more nearly correct for the minimum time.

Edwin W. Abrahamson

Chromatographic Reviews. Progress in Chromatography, Electrophoresis and Related Methods. Volume 2. Edited by M. LEDERER. Elsevier Publishing Company, 1960. pp. viii +195. 46s.

JUST as volume 1 of this compilation contained review articles which were published in the Journal of Chromatography during 1958, the present volume contains reviews which appeared in the Journal during 1959. The six reviews reprinted are:

Review of Gas-Liquid Chromatography (43 pp. 619 references) by C. J. Hardy and F. H. Pollard (Bristol),
Starch Electrophoresis: I. Starch Block Electrophoresis (15 pp. 62 references) by H. Bloemendal (Amsterdam),
Paper Chromatography of Dinitrophenylamino Acids (45 pp. 100 references) by G. Biserte *et al.* (Lille),
The Chromatography of the Flavanoid Pigments (24 pp. 91 references) by J. B. Harborne (Hertford),
The Separation of Different Types of Human Haemoglobin (42 pp. 84 references) by H. K. Prins (Amsterdam), and
Inorganic and Precipitation Chromatography (20 pp. 211 references) by E. Hayek (Innsbruck).

The paper by Biserte *et al.*, originally printed in French, has been translated into English, as has Hayek's review, which first appeared in German.

A critical discussion of six reviews on such widely differing aspects of chromatography is clearly beyond the scope of a single reviewer. Commenting in general terms only, the articles are comprehensive within the limitations of their size and they are sufficiently well referenced to be of value to all workers interested in the topics discussed. The literature coverage is commendably up-to-date, bearing in mind the initial date of publication; but inevitably in a subject of such rapid growth the reviews have become outdated in certain aspects during the year pending unrevised re-issue. For example, in gas-liquid chromatography, the now established use of capillary or open tubular columns and ionisation detectors gains only cursory mention in Hardy and Pollard's paper.

The volume is well produced and is adequately indexed. The text is relatively free from errors as is to be expected for a second printing, but a few mistakes remain, *e.g.* "carbon monoxyde" on p. 131 and on p. 174 "ensuring" should presumably read "ensuing".

It is noted in the editor's preface that subsequent volumes of Chromatographic Reviews may not be entirely devoted to reviews previously published in the Journal of Chromatography. Such a change in policy is to be applauded; indeed it can be cogently argued that the wide, amorphous and rapidly expanding subject of chromatography could be better served by reserving Chromatographic Reviews entirely for original reviews not outdated as a result of prior publication elsewhere. The price of the present volume is high for reviews which have already been published, though the translations will be valuable to a number of chromatographic specialists.

J. K. FOREMAN

Optische Daten zur Bestimmung anorganischer Substanzen mit dem Polarisations-Mikroskop. ERNST KORDES. Verlag Chemie, Weinheim, 1960. Pp. xi +192, with 8 separate Tables. DM 43.—.

THIS work will undoubtedly prove a valuable reference book for the practising chemical microscopist. It presents, systematically arranged, the optical properties of more than 1200 isotropic, uniaxial and biaxial inorganic materials, together with other properties (crystal form and habit, colour, melting point, hardness, solubility, density) that are of value in the identification of microscopic samples. Literature references are included for each substance.

In addition, the optical properties are arranged in condensed tabular form, and are also presented graphically as a series of separate folded diagrams contained in a pocket in the back cover.

The value of the book is enhanced by the provision of two admirable colour plates, showing the various types of interference figures, and by a really excellent summary, some twenty pages long, of the methods for determining optical properties using the polarising microscope. This last, although not full enough to satisfy a reader not already familiar with the principles of chemical microscopy, is nevertheless an excellent *aide memoire* or short "revision course" for anyone who has been out of practice with the methods for some time.

The author is to be congratulated on his work in collecting together and presenting in a single volume this mass of data which was previously scattered throughout a whole series of reference books, not all of them readily available. This book is for the chemist virtually an accessory to the polarising microscope.

CECIL L. WILSON

Crystals and the Polarising Microscope: A Handbook for Chemists and Others. Third Edition. N. H. HARTSHORNE and A. STUART. Edward Arnold (Publishers) Ltd., London, 1960. Pp. xv + 557. 80s.

THIS book needs no introduction to chemists who have occasion to use the microscope, the earlier editions having established it securely as a classical contribution to the field of chemical microscopy. The fact that the present edition contains some hundred pages more than the second edition is some indication of the extent to which it has been revised, although the alterations are to a large extent in detail rather than identifiable as substantial additions. Special mention may be made, however, of the sections dealing with the mechanism of crystal growth, of the chapter dealing with the construction and use of the polarising microscope, of the inclusion of fusion methods, and of the additions to the applications, particularly with reference to fibres. Various rearrangements of material have also been made. These and similar alterations only serve to make the book even more valuable than it already was.

For anyone who wishes to keep completely up-to-date in this field, the new edition is essential, and can be thoroughly recommended.

CECIL L. WILSON

Talanta, 1961, Vol. 8, pp. 368 to 370. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged:

Friday 9 *June* 1961: **Society for Analytical Chemistry,** Biological Methods Group: Summer visit to the Biological Laboratories, Research and Standards Departments, Boots Pure Drug Co. Ltd., Nottingham.

Wednesday 21 *June* 1961: **Society for Analytical Chemistry,** Microchemistry Group: Discussion Meeting. *The Feathers*, Tudor Street, London, E.C.4. 6.30 p.m.

The eighty-seventh Annual General Meeting of the Society for Analytical Chemistry was held at Burlington House, London, W.I., on Friday, 3 March, 1961, with the President, Mr. R. C. Chirnside, in the Chair.

The following Officers and Members of Council were elected for the forthcoming year:

President:	A. J. Amos
Past Presidents serving on the 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:	D. M. W. Anderson, B. Bagshawe, E. Bishop, S. G. Burgess, R. A. Chalmers, D. C. Garratt, S. H. Jenkins, E. Q. Laws, W. M. Lewis, C. A. Parker, D. W. Wilson, J. T. Yardley.
Ex-Officio Members of Council:	J. Markland (Chairman, North of England Section), A. F. Williams (Chairman, Scottish Section), G. V. James (Chairman, Western Section), H. C. Smith (Chairman, Midlands Section), C. Whalley (Chairman, Microchemistry Group), G. W. C. Milner (Chairman, Physical Methods Group), J. S. Simpson (Chairman, Biological Methods Group).

The sixteenth Annual General Meeting of the Biological Methods Group of the Society for Analytical Chemistry was held on Thursday 8 December 1960 in *The Feathers*, Tudor Street, London, E.C.4. The Chairman of the Group, Dr. J. I. M. Jones, F.R.I.C. presided.

The following were elected Officers of the Group for the forthcoming year:

Chairman: Mr. J. S. Simpson
Vice-Chairman: Mr. W. A. Broom
Hon. Secretary and Treasurer: Mr. K. L. Smith, Standards Department, Boots Pure Drug Co., Ltd., Nottingham, England.

The thirty-sixth Annual General Meeting of the North of England Section of the Society for Analytical Chemistry was held at the *Nag's Head Hotel*, Lloyd Street, Manchester, on Saturday, 28 January, 1961. The Chairman of the Section, Dr. J. S. Edisbury, presided.

The following were elected Officers of the Section for the forthcoming year:

Chairman: Mr. J. Markland
Vice-Chairman: Mr. C. J. House
Hon. Secretary and Treasurer: Mr. B. Hulme, Ch. Goldrei, Foucard and Son Ltd., Brookfield Drive, Liverpool, 9.

The twenty-sixth Annual General Meeting of the Scottish Section of the Society for Analytical Chemistry was held at the *Grosvenor Restaurant*, Gordon Street, Glasgow, on Thursday, 26 January, 1961. The Chairman of the Section, Mr. A. N. Harrow, presided.

The following were elected Officers of the Section for the forthcoming year:

Chairman: Mr. A. F. Williams
Vice-Chairman: Dr. R. A. Chalmers
Hon. Secretary and Treasurer: Mr. J. Brooks, Research and Development Department, I.C.I. Ltd., Nobel Division, Stevenston, Ayrshire.

The sixth Annual General Meeting of the Midlands Section of the Society for Analytical Chemistry was held at Regent House, St. Philips Place, Birmingham, on Tuesday, 14 March, 1961. The Chairman of the Section, Dr. S. H. Jenkins, presided.

The following were elected Officers of the Section for the forthcoming year:

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

The following new British Standards are announced in B.S.I. News:

B.S. 1121: *Methods for the analysis of iron and steel: Part* 42: 1961: *Cobalt in iron and steel.* This specifies a method for the photometric determination of trace amounts of cobalt in commercially-pure iron and all types of steel containing cobalt within the range 0·002% to 0·04% of cobalt. (Price 3s.)

B.S. 1748: *Methods for the analysis of copper alloys: Parts* 1–5: 1961: *Methods for the determination of copper, lead, iron, aluminium and nickel in copper alloys.* This specifies reagents required, recommended methods of sampling and test procedure from one sample weighing for the determination of copper, lead, iron, aluminium and nickel, in copper alloys containing 1 to 14% of tin, 1 to 2% of nickel, and small amounts of aluminium, *e.g.* phosphor bronzes, leaded phosphor bronzes, gun metals and leaded gun metals. (Price 6s.)

B.S. 3334: 1961: *Method for the quantitative chemical analysis of mixtures of cellulose triacetate and secondary cellulose acetate fibres.* This provides a method for determining the proportions of the two components in mixtures of these fibres. It is based on dry-weights but a formula is also given for reporting the results including additions to compensate for moisture.

The method is suitable for application to fibres in any textile form, *i.e.* tow, sliver, roving, yarn or fabric. (Price 4s.)

B.S. 3336: 1961: *Method for the quantitative chemical analysis of ternary mixtures of protein fibres, polyamides and certain other fibres.* This provides a method for determining the proportions of the three components in mixtures of these types of fibres.

Formulae are given for expressing the results either on the basis of dry-weights or of corrected invoice weights.

The method is suitable for application to fibres in any textile form, *i.e.* tow, sliver, roving, yarn or fabric. (Price 3s.)

B.S. 3338: *Methods for the sampling and analysis of tin and tin alloys: Part I:* 1961: *Sampling of ingot tin.* This specifies sampling of ingots, preparation of surfaces, method of taking samples by means of sawing, and precautionary measures against contamination of the sawings. (Price 3s.)

Part 2: 1961: *Tin in ingot tin (aluminium reduction method).* This specifies reagents required, recommended methods of sampling and test procedure for the determination of tin in ingot tin having a tin content from 99·0 to 99·8%. (Price 4s.)

Part 7: 1961: *Silver in solders (volumetric: ammonium thiocyanate method).* This specifies reagents required, recommended methods of sampling and test procedure for the determination of silver in solders having a silver content up to 3%. (Price 3s.)

Part 11: 1961: *Tin in solders (nickel coil reduction method).* This specifies reagents required, recommended methods of sampling and test procedure for the determination of tin in solders having a tin content exceeding 1%. (Price 3s.)

Part 12: 1961: *Sampling of solders.* This specifies selection of ingots, bars, sticks or wire, preparation of sample, preparation of surfaces, methods of taking final samples by means of sawing, as well as precautionary measures against contamination of the sawings. (Price 3s.)

B.S. 3344: 1961: *Method for the quantitative chemical analysis of binary mixtures of cellulose triacetate and certain other fibres.* This provides a method for determining the proportions of the two components in mixtures of these fibres. It is based on dry-weights but a formula is also given for reporting the results including additions to compensate for moisture. The method is suitable for application to fibres in any textile form, *i.e.*, tow, silver, roving, yarn or fabric. (Price 4s. 6d.)

The following revised British Standard is announced:

B.S. 1583:1961: *One-mark pipettes.* Thirteen sizes of pipette from 0·5 ml to 200 ml are specified, all being of the bulb pattern except that the 0·5-ml size is a straight pipette and that both bulb and straight patterns are permitted for Classes A and B pipettes of the 1-ml size and Class B pipettes only of the 2-ml size. Full dimensions are given but only the essential ones are listed as mandatory, the remainder being given for the guidance of manufacturers. Standard methods are included for the determination of capacity and delivery time and tolerances are listed for both. (Price 4s.)

The following amendment slip is announced:

B.S. 1016: *Methods for the analysis and testing of coal and coke: Part* 12: 1959: *Caking and swelling properties of coal. Amendment No.* 1: *PD* 4005. (Gratis)

Part 15: 1960: *Fusibility of coal ash and coke ash. Amendment No.* 1: *PD* 4004. (Gratis)

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PAPERS RECEIVED

Analytical applications of the reagent Arsenazo-III: Determination of thorium, zirconium and rare-earth elements: S. B. Savvin. (22 *February* 1961).

Studies on uronic acid materials—III: The use of ^{14}C compounds to determine acid decarboxylation reaction times: D. M. W. Anderson and S. Garbutt. (4 *March* 1961).

The determination of thiol compounds. J. M. Bakes and P. G. Jeffery. (6 *March* 1961).

Estimation of xanthate and dixanthogen: S. Ramachandra Rao. (6 *March* 1961).

Photometric titrations—II: Design and construction of a photometric titrator: H. Flaschka and P. Sawyer. (6 *March* 1961).

Determination of radiophosphorus by solvent extraction. Harley H. Ross and Richard B. Hahn. (2 *March* 1961).

Isotopic dilution analysis by ion-exchange: Determination of traces of iron: Jiří Starý and Jaromír Růžička. (10 *March* 1961).

Spectrographic analysis of gallium and indium with extraction: Jerzy Minczewski, Hanna Maleszewska and Teresa Steciak. (11 *March* 1961).

Spectrophotometric and potentiometric studies on the composition of iron complexes of potassium octacyanomolybdates: Wahid U. Malik and S. Iftikhar Ali: (14 *March* 1961).

The determination of rhenium in rocks by neutron-activation analysis: D. F. C. Morris and F. W. Fifield. (14 *March* 1961).

Der Aufbau einiger Metall-Carbamatverbindungen: H. Malissa and H. Kolbe. (15 *March* 1961).

Coulometric titration by electrogenerated stannous ion: Takeo Takahashi and Hiroshi Sakurai. (15 *March* 1961).

Coulometric titration of hydroxylamine and hydrogen peroxide by electrogenerated ceric ion: Takeo Takahashi and Hiroshi Sakuria. (20 *March* 1961).

Spectrophotometric determination of bismuth with Xylenol Orange after Dithizone-chloroform extraction: Hiroshi Onishi and Nasumi Ishiwatari. (20 *March* 1961).

Spectrophotometric determination of vanadium with 3,3′-diaminobenzidine: K. L. Cheng. (24 *March* 1961).

Sur un principe de colorimétrie en milieux non-aqueux—III: L'emploi du chlorure de p-nitrophénylazo benzoyle pour le dosage des amines primaires et sécondaires: Jaroslav Bartos. (24 *March* 1961)

5-Amino-2-benzimidazolethiol as an analytical reagent—I: Spectrophotometric determination of palladium. J. G. Sen Gupta. (27 *March* 1961).

NOTES FOR CONTRIBUTORS

1. General

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

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

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

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

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

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

2. Script Requirements

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

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

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

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

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

▲ △ ⊡ □ ● ○ ◬ ⊙ ⊕ ⊖ ⌽ ⊗

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

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

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[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.

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