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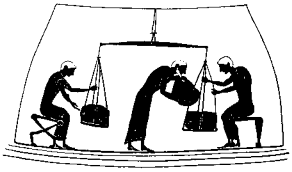

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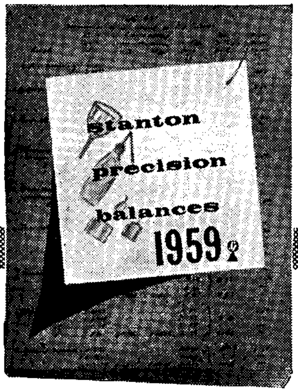
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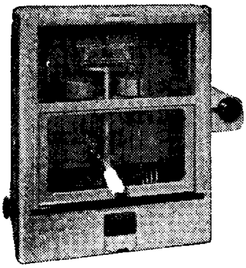

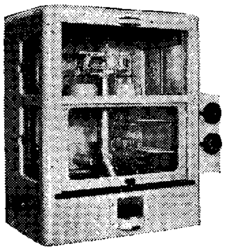

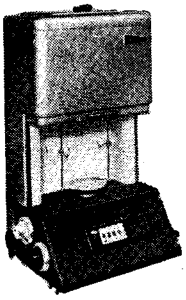

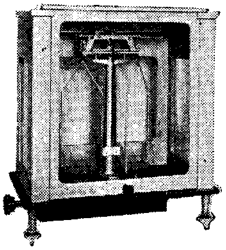

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Incidental information

No.13

Items of interest from our laboratory notebooks

▶ Most analysts know about 1:10-phenanthroline and many use it for iron determinations. Not so many people seem to know that **4:7-diphenyl-1:10-phenanthroline** is twice as sensitive as 1:10-phenanthroline in the colorimetric determination of iron. There are several papers on the subject but the latest is *Analyst*, 1958, **83**, 80. The reagent is also called **Bathophenanthroline**, and we make it.

▶ Then, again the substitution of methyl groups in the 2:9 positions has the interesting effect of making the reagent insensitive to iron and we then have a selective and sensitive reagent for copper (see *Anal. Chem.*, 1956, **28**, 1158). Hopkin & Williams make **2:9-dimethyl-1:10-phenanthroline** (sometimes called **Neocuproin**).

▶ One does not think of sulphate as a radical one can determine absorptiometrically, but this is now possible for low concentrations. **Barium chloranilate** is the reagent and there are two papers on the subject—*Anal. Chem.*, 1957, **29**, 281 and *Anal. Chem.*, 1958, **30**, 202. Hopkin & Williams make it.

▶ Hopkin & Williams Ltd. were also early off the mark with supplies of the remarkable new colour-producing reagent for fluoride ions, **3-aminomethylalizarin-NN-diacetic acid**, described by Belcher, Leonard and West (*Talanta*, 1959, **2**, 92.) This important reagent is already available from stock.

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ARGENTOMETRISCHE TITRATIONEN MIT REDOXINDICATION—II

BESTIMMUNG VON AMMONIAK, AMMONIUM-IONEN UND STICKSTOFFHALTIGEN ORGANISCHEN SUBSTANZEN

L. ERDEY, K. VIGH und L. PÓLOS
Institut für Allgemeine Chemie der Technischen Universität Budapest, Ungarn

(*Received* 1 *January* 1959, *Revised paper received* 16 *May* 1959)

Zusammenfassung—Es wurde ein Verfahren zur massanalytischen Ammoniakbestimmung ausgearbeitet. Das Ammoniak wird mit Natriumtetraphenylborat gefällt, und dessen acetonhaltige Lösung in Anwesenheit von Variaminblau als Redoxindicator mit Silbernitratmasslösung titriert. Die Titration lässt sich auch auf indirektem Wege, durch Messung der überschüssigen Tetraphenylborationen durchführen.

Die Methode wurde auch auf die Stickstoffbestimmung in organischen Stoffen ausgebreitet, indem nach der Kjeldahlschen Zerstörung der Stickstoff direkt im Zerstörungsrückstand bestimmt wurde.

DAS Natriumtetraphenylborat wurde zuerst von Wittig und Mitarbeitern[1] als analytisches Reagens angewandt. Raff und Brotz[2] arbeiteten die gewichtsanalytische Bestimmung der Kalium- während Kohler[3] die der Ammoniumionen aus. Die argentometrische Titration des in Aceton gelösten Kaliumtetraphenylboratniederschlages wurde von Rüdorff und Zannier,[4] weiterhin von Hahn[5] ausgearbeitet, u.zw. in Anwesenheit von Eosin bzw. Kaliumchromat als Indicator. Das Verfahren mit Eosin ist als eine Differentialtitration zu betrachten, da Eosin nur nach Zugabe von bekannter Menge an Kaliumbromid als Indicator funktioniert. Kaliumchromat ist indessen in acetonhaltiger Lösung ein nicht genügend empfindlicher Indicator. In einer früheren Mitteilung[6] berichteten wir über die argentometrische Titration von Kaliumtetraphenylborat in Anwesenheit von Variaminblau, als Indicator. Diesen Indicator fanden wir auch bei der Bestimmung der Ammoniumionen als gut geeignet. Wir breiteten die Methode auch auf die Stickstoffbestimmung von stickstoffhaltigen und mit Kjeldahl Verfahren zerstörbaren organischen Verbindungen aus.

Die Fällung der Ammoniumionen mit Lithium- oder Natriumtetraphenylborat (Kalignost) lässt sich entweder in neutraler oder in saurer Lösung vornehmen. Das pH der Lösung ist zwischen 1 und 6,5 einzustellen.

EXPERIMENTELLER TEIL

Lösungen

0,05 *n Silbernitratlösung*. 8,4944 g des handelsüblichen, anal. reinen Silbernitratpräparats werden in Wasser auf 1 Liter gelöst.

Acetonhaltige 0,05 *n Silbernitratlösung*. Eine 0,1 n Silbernitratlösung wird mit Aceton genau auf doppeltes Volumen verdünnt.

0,1 *m Natriumtetraphenylborat-Fällungsreagens* 3 g des handelsüblichen Natriumtetraphenylborats (Kalignost) werden in 100 ml Wasser gelöst. Um die etwas trübe Lösung zu klären wird sie mit 0,5 g Aluminiumoxyd versetzt, 5 Minuten lang umgeschüttelt und sodann durch ein dichtes Filtrierpapier filtriert. Der erste Einzelteil des Filtrats wird auf das Filtrier-papier zurückgeschüttet

Die Lösung ist höchstens 3 Tage lang brauchbar. 0,6 ml Fällungsreagens entspricht 1 mg NH_4^+.

Waschflüssigkeit. Der Ammoniumtetraphenylboratniederschlag wird nach der weiter unten folgenden Arbeitsvorschrift (*a*) bereitet. Dem mit Wasser gründlich ausgewaschenen Niederschlag werden 0,1–0,2 g Mengen entnommen und in 1 Liter Wasser 25 min lang geschüttelt. Um die Lösung zu klären werden 2–3 g anal. reines Aluminiumoxyd zugefügt. Die Lösung wird sodann wieder 5 Minuten lang umgeschüttelt und schliesslich durch dichtes Filtrierpapier filtriert.

1 %-*iger Variaminblauacetatindicator.* 0,2 g des handelsüblichen Variaminblau B-präparats werden unter gründlichem Verreiben in einem Mörser in 20 ml Wasser gelöst. Die Lösung wird in einen 100 ml Scheidetrichter gebracht, mit einer Messerspitze Ascorbinsäure reduziert und mit Hilfe von 5 ml 1 n Natriumhydroxydlösung wird die schwerlösliche Variaminblau Base gefällt. Die niederschlaghaltige Flüssigkeit wird mit 20 ml Benzol zusammengeschüttelt und die Benzolschicht in einen anderen Scheidtrichter abgelassen. Da vermischt man dieselbe mit 20 ml 20%-iger Essigsäurelösung und die Variaminblau Base wird damit wieder—nun aber schon als essigsaures Salz—in die wässrige Phase gebracht. Als Indicator wird diese abgesonderte essigsaure Lösung gebraucht. Aus dieser Indicator-lösung wenden wir zu einer Titration 2–3 Tropfen an.

(*a*) *Arbeitsverfahren in Abwesenheit von Schwermetallionen*

Die etwa 5–50 mg (am günstigsten 20–50 mg) Ammoniumionen enthaltende beinahe neutrale Lösung wird mit Wasser dermassen verdünnt, dass auf 1 mg NH_4^+ etwa 8 ml des Lösungsvolumens entfallen. Sodann wird die Lösung pro 50 ml Lösungsvolumen mit je 1 ml 0,1 n Essigsäurelösung versetzt (pH = 3–5), und unter beständigem Rühren werden die Ammoniumionen mit 0,1 m Natriumtetraphenylboratlösung kalt gefällt. Vom Fällungsreagens wird ein etwa 50%-iger Überschuss angewandt, d.h. auf jedes mg NH_4^+ wird insgesamt 1 ml Fällungsreagens gerechnet. Die niederschlaghaltige Flüssigkeit wird sodann wenigstens auf 5 min beiseitegestellt und nachher durch feinporösiges Filterpapier filtriert. Der Niederschlag wird mit etwa 50 ml Waschflüssigkeit in 4–6 Teilen dekantiert und samt Filterpapier in das Becherglas zurückgebracht. Sodann werden je nach der Menge des Niederschlages 6–60 ml Aceton zugefügt und löst darin unter Umrühren mit einem Glasstäbchen den Niederschlag auf. Nach Zugabe von 1 ml 2 n Essigsäurelösung und 2–3 Tropfen Variaminblauacetatindicator titriert man die Lösung unter beständigem Umrühren mit einer 0,05 n Silbernitratmasslösung bis zum Erscheinen der violetten Farbe. Die Anwesenheit des Filterpapiers stört die Titration nicht. Gegen Ende der Titration soll man nach Zugabe jeden einzelnen Tropfens der Masslösung ungefähr 15–30 sec die niederschlaghaltige Flüssigkeit kräftig umrühren. 1 ml 0,05 n Silbernitratmasslösung entspricht 0,8515 mg NH_3, 0,9020 mg NH_4^+ bzw. 0,7004 mg N.

Bemerkungen. Zur Überprüfung der Methode wurde aus p.a. Ammoniumchlorid durch genaue Einwaage eine Stammlösung bereitet deren Einzelteile nach obiger Arbeitsvorschrift titriert wurden. Die Ergebnisse weichen vom Sollwert bei der Bestimmung von 13 mg Ammoniumchlorid um −0,97 %, und bei der Bestimmung von 133 mg Ammoniumchlorid um +0,01 % ab. Bei der Bestimmung von 27 mg Ammoniumchlorid aus 6 Paralleltitrationen wurde die Standarddeviation und die Abweichung vom Sollwert festgestellt. Die Abweichung vom Sollwert betrug −0,17 % und die Standarddeviation ±0,11 %.

Arbeitsverfahren in Anwesenheit von Schwermetallionen

J. H. Cluley[7] beseitigte die störende Wirkung der fremden Metallionen bei der Bestimmung von Kaliumionen mit Tetraphenylborat durch Fällung entweder in stark saurem Medium (pH ∼ 2) oder in Anwesenheit von Natriumäthylendiamintetraacetat Na_2-EDTA in einer beinahe neutraler Lösung (pH ∼6,5). Laut unserer Versuche lässt sich unter diesen Versuchsumständen die störende Wirkung der Fremdionen auch bei der Ammoniumbestimmung beseitigen. K, Rb, Cs, Ag, Hg(I), Hg(II) und Th(IV) wirken aber auch in diesem Falle störend ein. In Anwesenheit dieser Ionen muss man das Ammoniak aus alkalischer Lösung abdestillieren bzw. man soll die weiter unten angegebene indirekte Bestimmungsmethode (d) anwenden.

(*b*) *Fällung in stark saurer Lösung.* Die etwa 5–50 mg Ammoniumionen enthaltende, beinahe neutrale Lösung wird mit Wasser derart verdünnt, dass auf 1 mg NH_4^+ 8 ml des Lösungsvolumens entfallen, und sodann mit soviel 0,1 n Salzsäure versetzt, dass deren Menge ein Zehntel des Lösungsvolumens betrage. Das pH der Lösung stellt sich derart auf etwa 2 ein. Im weiteren führt man Fällung, Filtration, Auswaschen und Titration wie im Abschnitt (a) bereits beschrieben, aus.

(*c*) *Fällung in Anwesenheit von* Na_2-EDTA. Die etwa 5–50 mg Ammoniumionen und höchstens

100 mg Schwermetallionen enthaltende Lösung wird mit 1 g Na_2-EDTA versetzt und nach dessen Auflösung in Anwesenheit von 2 Tropfen 0,04%-iger Chlorphenolrotindicatorlösung mit 1 n Natriumhydroxydlösung bis zum Farbumschlag von Gelb nach Rot (pH = 6,5) neutralisiert. Die Lösung wird sodann mit destilliertem Wasser derart verdünnt, dass auf jedes mg NH_4^+ 8 ml des Lösungsvolumens entfalle. Fällung, Filtration, Auswaschen und Titration führt man wie im Abschnitt (a) bereits beschrieben, aus.

Die Ergebnisse beweisen, dass die Bestimmung lässt sich in Anwesenheit von Mg, Ca, Ba, Zn, Pb, Al, Fe(III), Cu, Co, Mn(II), Ni, Cr(III), Ti(IV), As(III) und Sb(III) mit gutem Erfolg durchführen.

TABELLE I

Methoden	Carbamid Einwaage, *g*	Theoretischer N-gehalt, *mg*	Verbrauch an		N gefunden *mg*	Abweichung vom Sollwert	
			0,1 n HCl, *ml*	0,05 n $AgNO_3$, *ml*		*mg*	%
Verfahren nach Kjeldahl	0,2200	102,63	14,69 14,63 14,67		102,67	+0,04	+0,04
Direkte Ammoniumbestimmung im Zerstörungsrückstand	0,1775	82,80		23,61 23,64 23,62	82,71	−0,09	−0,10
Indirekte Ammoniakbestimmung im Zerstörungsrückstand	0,2500	116,62		33,18 33,21 33,15	116,19	−0,43	−0,36

(*d*) *Bestimmung neben K-, Rb- und Cs-Ionen.* Das Ammoniak wird von den begleitenden Schweralkalimetallionen durch Destillation in alkalischem Medium getrennt. Als Absorptionsflüssigkeit dient entweder überschüssige Salzsäure-, Schwefelsäure- oder 40 ml gesättigte Borsäurelösung. Das im Recipienten aufgefangene Ammoniak wird gemäss Arbeitsverfahren (a) bestimmt. Die Fällung lässt sich aus der borsauren Lösung direkt, ohne Einstellung des pH durchführen.

Bestimmung von Ammoniumionen durch Rücktitration

Die Bestimmung der Ammoniumionen lässt sich auch durch Titration des im Überschuss angewandten Natriumtetraphenylborats ausführen. In diesem Falle muss man das Fällungsreagens in bekannter Menge und von bekanntem Wirkungswert anwenden. Der Niederschlag muss durch Filtrieren entfernt werden, weil die Titration in Anwesenheit von Kaliumtetraphenylborat nicht durchgeführt werden kann, da sich das Silbertetraphenylborat schlechter löst als das Kaliumtetraphenylborat, was einen Überverbrauch an Masslösung bewirkt. Das Natriumtetraphenylborat enthaltende Filtrat muss auch mit Aceton mindestens von gleichem Volumen versetzt werden, denn sonst fällt der Variaminblauindicator als Variamintetraphenylboratniederschlag aus.

Titerbestimmung der 0,1 *m Natriumtetraphenylboratlösung.* 10,00 ml des 0,1 m Natriumtetraphenylborat-Fällungsreagens werden mit 1 ml 2 n Essigsäure, 11 ml Aceton und 2–3 Tropfen Variaminblauacetat versetzt. Die Lösung wird sodann mit 50 Volumenprozent enthaltender, 0,05 n Silbernitratlösung titriert. (Eine 0,1 n Silbernitratlösung von bekanntem Wirkungswert wird mit Aceton genau aufs Doppelte verdünnt). Gegen Ende der Titration wird nach jedem Tropfen der zugefügten Masslösung 15–20 sec gewartet. Der Endpunkt der Titration wird durch Erscheinen der violetten Farbe des oxydierten Variaminblaus bekanntgegeben.

Die Titration lässt sich auch mit wässriger 0,05 n Silbernitratmasslösung durchführen, in diesem Falle muss man aber die zu titrierende Lösung mit soviel Aceton versetzen, dass deren Acetongehalt beim Endpunkt der Titration mehr als 50 Volumenprozent beträge. Die zu titrierende Lösung darf natürlich keine Chloridionen enthalten.

(e) *Arbeitsvorschrift für das indirekte Verfahren.* Die zu bestimmende etwa 5 mg Ammoniumionen enthaltende Ammoniumsulfat- oder Ammoniumnitratprobe wird in einen 100 ml Messkolben eingewogen, mit 10 ml 0,1 n Essigsäurelösung versetzt und mit Wasser auf etwa 40 ml verdünnt. Unter beständigem Umschütteln des Kolbens werden 50,00 ml 0,1 m Natriumtetraphenylboratlösung in den Kolben pipettiert, welchen man sodann mit Wasser bis zur Marke auffüllt. Nach Zusammenschütteln lässt man die niederschlaghaltige Flüssigkeit etwa 5 min stehen und filtriert durch trockenes Filtrierpapier in einen trockenen Kolben. Das erste Detail des Filtrats wird weggeworfen. Aus dem weiteren Filtratteilen werden 25,00 ml auspipettiert, mit 1 ml 2 n Essigsäurelösung und 25 ml Aceton versetzt und in Anwesenheit von 2–3 Tropfen Variaminblauacetat als Indicator mit 50% Aceton bereiteter 0,05 n Silbernitratlösung titriert. Das Vierfache des Masslösungsverbrauches substrahiert man vom Volumen der mit dem eingewogenen 50,00 ml 0,1 m Natriumtetraphenylborat äquivalenten 0,05 n Silbernitratmasslösung. Aus dieser Differenz ergibt sich die den Ammoniumionen entsprechende Menge der 0,05 n Silbernitratlösung. Die Titration lässt sich auch bei diesem Verfahren mit wässriger 0,05 n Silbernitratlösung ausführen, in diesem Falle muss man aber die zu titrierende Lösung mit soviel Aceton versetzen, dass der Acetongehalt der Lösung im Endpunkt der Titration mindestens 50 Volumenprozent betrage.

Tabelle II

Untersuchte Substanz	Theoretischer N-gehalt, mg	Verbrauch an 0,05 n $AgNO_3$-1sg ml	Mittelwert N gefunden,		Abweichung vom Sollwert,	
			ml	*mg*	*mg*	%
Carbamid	16,55	23,64 23,66 23,64	23,64	16,55	±0,0	±0,0
Carbamid	23,34	33,14 33,18 33,14	33,16	23,23	−0,11	−0,47
Sojamehl	13,16	18,56 18,68 18,70	18,64	13,05	−0,11	−0,83
Eiweiss (getrocknet)	5,05	7,20 7,16 7,22	7,18	5,02	−0,03	−0,60

Unsere mit obiger Methode erhaltenen Ergebnisse zeigen eine +0,84%-ige Abweichung vom Sollwert bei der Bestimmung von 32 mg Ammoniumsulphat und eine −0,24%-ige bei der Bestimmung von 130 mg Ammoniumsulphat. Die Genauigkeit der Methode und ihre Standarddeviation wurde aus 6 Paralleltitrationen von 130 mg Ammoniumsulphat bestimmt. Die Abweichung vom Sollwert ergab sich zu −0,19%, während die Standarddeviation ±0,19% betrug. Die Resultate der Rücktitration weichen vom Sollwert besser ab als die der direkten Titration.

Sämtliche oben beschriebene argentometrische Ammoniumbestimmungsverfahren sind günstiger als das übliche Destillationsverfahren, da bei der Durchführung derselben keine Destillationsapparatur benötigt wird und die aus der Destillationsmethode hervorgehenden sämtlichen Fehler dabei beseitigt werden. Ein weiterer Vorteil der neuen Verfahren besteht darin, dass die Bestimmung sich auf eine sehr spezifische Reaktion gründet, auf die genaue Einstellung des pH nicht empfindlich ist und schliesslich sehr genaue Ergebnisse liefert.

ARGENTOMETRISCHE TITRATION VON STICKSTOFFHALTIGEN ORGANISCHEN STOFFEN

Die rasche Bestimmungsmöglichkeit der Ammoniumionen legte den Gedanken nahe den Stickstoffgehalt von organischen Substanzen nach der Kjeldahlschen Zerstörung direkt im Zerstörungsrückstand ohne Destillation zu bestimmen. Es liegen nach der Zerstörung zwei Möglichkeiten zur Bestimmung des entstehenden Ammoniaks vor. Der ersten Methode gemäss wird das Ammoniak auf oben beschriebene Art—Verfahren (*a*)(*d*)—nach Fällung, Filtration, Auswaschen und Auflösung in Aceton mit Silbernitratmasslösung titriert. Nach der anderen Methode—Verfahren (*e*)—wird die das zu bestimmende Ammoniak enthaltende Lösung quantitativ in einen Messkolben gebracht, wo man das Ammoniak mit bekannter Menge Natriumtetraphenylborat fällt. Nach Auffüllen des Kolbens und Abfiltrieren eines aliquoten Teils wird der Natriumtetraphenylboratüberschuss titriert. Daraus wird so dann der Stickstoffgehalt bestimmt.

Um die Methode zu kontrollieren bestimmten wir den Stickstoffgehalt von Carbamid sowohl mit Hilfe des Kjeldahlverfahrens mit acidimetrischer Endpunktsanzeige als auch mit unseren argentometrischen direkten und indirekten Verfahren. Laut Angaben der Tabelle II sind die Ergebnisse von befriedigender Genauigkeit. Über die Genauigkeit von einigen Stickstoffbestimmungen in organischen Stoffen gibt Tabelle II Aufklärung.

Summary—The authors have developed a new method for the titrimetric determination of ammonia. Ammonia is precipitated by means of potassium tetraphenylboron and its solution in acetone is titrated with standard silver nitrate solution in the presence of Variamin Blue acetate as indicator. The titration can also be carried out indirectly by measuring the excess of tetraphenylboron.

This method can also be used to determine nitrogen in organic compounds after a Kjeldahl digestion.

Résumé—Les auteurs ont proposé une nouvelle méthode pour le dosage titrimétrique de l'ammoniaque. Celui-ci est précipité par le tetraphénylborure de potassium et sa solution dans l'acétone est titrée par une solution de nitrate d'argent étalon en présence de bleu d'acétate de variamine. Le titrage peut aussi être conduit indirectement en mesurant l'excès du tetraphenylborure.

Cette méthode peut aussi être utilisée pour déterminer l'azote dans des produits organiques après une minéralisation au kjeldahl.

LITERATUR

[1] G. Wittig, G. Keicher u. A. Rückert, *Liebigs Ann.*, 1949, **563,** 110.
[2] P. Raff u. W. Brotz, *Z. analyt. Chem.*, 1951, **133,** 241.
[3] M. Kohler, *Ibid.*, 1953, **138,** 9.
[4] W. Rüdorff u. H. Zannier, *ibid.*, 1952, **137,** 1.
[5] F. L. Hahn, *ibid.*, 1955, **145,** 97.
[6] L. Erdey, I. Buzás u. K. Vigh, *Talanta*, 1958, **1,** 377.
[7] H. J. Cluley, *Analyst*, 1955, **80,** 354.

Talanta, 1959, Vol. 3, pp. 6 to 13. Pergamon Press Ltd. Printed in Northern Ireland

ARGENTOMETRIC TITRATIONS BY MEANS OF REDOX INDICATION—III

DETERMINATION OF NITRATE IONS AND NITRO COMPOUNDS

L. ERDEY, L. PÓLOS
Institute for General Chemistry, Technical University, Budapest, XI, Hungary

and Z. GREGOROWICZ
Department of Inorganic Chemistry, Silesian Technological Institute,
Gliwice, Poland

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Summary—A new method for the determination of nitrate has been worked out. (*a*) Nitrate ions can be reduced to ammonia in acidic medium by means of *ferrum reductum* in the presence of nickel sulphate. Ammonia can be precipitated in acidic medium as ammonium tetraphenylboron. After filtering and washing, the precipitate can be dissolved in acetone and the solution can be titrated with silver nitrate with Variamin Blue acetate as indicator. (*b*) Nitrate ions can be reduced in alkaline medium with Devarda's alloy, the ammonia being distilled and titrated as described above. This method has been applied to the determination of nitrates accompanied by organic material, and of nitrozo, azo and diazo compounds.

THE most precise methods for the determination of nitrate are based on the reduction of nitrate ions to ammonia. These methods all have the same principle, namely ammonia formed by reduction is distilled from a neutral or alkaline medium, and the separated ammonia is titrated by alkalimetric methods or with sodium hypobromite.[1–4] Z. Szabó and his co-workers[5,6] carry out the reduction in the presence of silver ions with iron^{II} hydroxide as a reducing agent, and either titrate the iron^{III} ions formed, or back-titrate the remaining iron^{II} by redox methods after the separation of ammonia.

Work published up to the present does not offer a specific and satisfactorily precise method for the determination of ammonia formed by reduction from the nitrate ions. Excellent results which we obtained by titration of ammonium ions with sodium tetraphenylboron (Kalignost)[7] suggested the use of this precise and reasonably specific method for the determination of ammonia formed by the reduction of nitrate ions.

REDUCTION OF NITRATE IONS IN ACID MEDIUM BY MEANS OF METALS

Among methods using metals as reducing agents, the best known is that of Ulsch[1] who reduces the nitrate ions with "*ferrum reductum*". Although Martin also suggests the use of metallic zinc for the reduction,[8] the present authors, like Ulsch, were unable to obtain satisfactorily precise results with this method. To investigate the efficiency of the reduction parallel experiments were carried out with various common metals having different standard potentials. To a known amount of sodium nitrate was added an equivalent amount of the well-powdered metal, and the amount of ammonia formed by the reduction was measured. Under the conditions mentioned, metallic iron was found to be the best reducing agent. Using a 5–10 fold excess of the metal over the stoichiometric amount, in the case of iron the reduction is complete, but with the other metals smaller amounts of ammonia than calculated were always obtained. The amount of iron can be considerably reduced by the addition to the solution of nickel or cobalt sulphate as a catalyst.

Reagents

1. 0·1*N* *Silver nitrate standard solution* was prepared by weighing and dissolving 16·9888 g p.a. silver nitrate per litre. 0·01*N* and 0·05*N* solutions were made by appropriate dilution of the former.
2. 0·1*M* *Sodium tetraphenylboron* (*Kalignost*): a 3·5% solution was prepared in water, clarified with 0·5 g aluminium oxide for each 100 ml, and filtered through a thick filter. About 0·6 ml of this solution is equivalent to 1 mg NH_3. The solution is stable for some days.
3. *Wash solution:* a small amount of ammonium tetraphenylboron was precipitated, and washed thoroughly with distilled water. 0·1–0·2 g of the precipitate was suspended in 1 litre of distilled water, shaken for 25 minutes, clarified with aluminium oxide and filtered through a thick filter. The clear filtrate was used as a wash solution.
4. *Indicator solution: Variamin Blue acetate,* 1% *solution:* 0·2 g of commercial Varamin Blue dye (which is a hydrochloric acid salt of the base) was dissolved in 20 ml water and reduced by 0·5 g ascorbic acid. The solution was then rendered alkaline with 5 ml *N* sodium hydroxide and the precipitated free base was dissolved by shaking the solution with 20 ml benzene. The organic layer was separated, and shaken with 20 ml 20% acetic acid solution. The Varamin Blue acetate which formed was to be found in the acetic acid phase; the latter was used as an indicator. The indicator solution prepared by this way is stable for 3–4 weeks.
5. 0·2*M* *Disodium ethylendiamine tetra-acetate solution* (Na_2-EDTA) was prepared by dissolving 74·4 g Na_2-EDTA in water and dilution to 1 litre.
6. 0·2*M* *Sodium acetate solution:* 27·2 g sodium acetate was dissolved in water and diluted to 1 litre.

Procedure

The sample, which contained 1–120 mg of nitrate, was weighed in a 100-ml Kjeldahl flask; 0·5 g finely powdered "ferrum reductum," 0·3 g nickel sulphate and 15 ml 2*N* sulphuric acid were added. Into the neck of the flask a test tube with a ball blown in the middle part and containing water for cooling was placed. The mixture was gently heated with a micro-burner, and after 10 minutes the flame was regulated, so that the mixture was just boiling. Reduction was complete after 1 hour treatment and the iron was dissolved completely. After cooling the mixture was washed into a beaker; 10–15 ml of 0·2*M* sodium acetate solution and 60 ml 0·2*M* Na_2-EDTA solution were added. To this solution 0·1*M* sodium tetraphenylboron was added dropwise at room temperature until the reagent was in 50% excess. Precipitation was complete in 5 minutes. The precipitate was collected on a thick filter paper 7 cm in diameter, and was washed 5–6 times with small portions of wash-solution. The filter paper containing the precipitate was returned to the beaker, and was thoroughly stirred with acetone, using a glass rod. The acetone dissolved the precipitate. To the mixture (containing filter-paper-shreds) 1–2 ml 2*N* acetic acid and 1–2 drops of 1% Variamin Blue acetate indicator were added, and it was then titrated while shaking, against 0·1*N* or 0·01*N* silver nitrate solutions until a blue colour appeared. Near the end-point it was advisable to titrate slowly and to mix the solution well after each drop of the standard solution was added. The shreds of filter paper did not interfere. At the end-point the solution must contain at least 50% of acetone.

The method was controlled by analysing samples of nitrite-free sodium nitrate solution prepared from nitric acid, which was controlled acidimetrically. According to Table I, results are very accurate even in micro quantities. The accuracy and standard deviation were established by 11 parallel titrations in 0·01*N* solution. Results show that the method is very accurate, with a standard deviation of ±0·25%. In 0·1*N* solution, when greater amounts of nitrate were determined, the accuracy was even better.

The method can be combined with the distillation of ammonia. Distillation is recommended especially when potassium, thallium, thorium or mercury salts are present, or if other heavy metal salts are present in large quantities. After reduction the solution must be washed into a distillation apparatus, and rendered alkaline with sodium hydroxide. Ammonia can be then distilled. About 40 ml of saturated boric acid solution (4·9 g H_3BO_3 dissolved in 100 ml water) or an excess of sulphuric acid is placed in the collector flask. After neutralisation of the strong acid (boric acid must not be neutralized) ammonium tetraphenylboron can be precipitated. In this case Na_2-EDTA should not be added since precipitation of ammonia with sodium tetraphenylboron is highly specific.

TABLE I.—ACCURACY OF THE TITRATION AS A FUNCTION OF THE AMOUNT OF NITRATE

0·01*N* HNO_3 taken, *ml*	0·01*N* $AgNO_3$ consumed, *ml*	Average, *ml*	Difference	
			ml	%
9·94	9·76 9·84 9·81	9·80	−0·14	−1·4
14·88	14·88 14·80 14·83	14·84	−0·04	−0·26
24·85	24·76 24·78 24·81	24·78	−0·07	−0·28

0·1*N* HNO_3 taken, *ml*	0·1*N* $AgNO_3$ consumed, *ml*	Average, *ml*	Difference	
			ml	%
4·97	4·97 4·95 4·95	4·96	−0·01	−0·2
9·94	9·89 9·92 9·95	9·92	−0·02	−0·20
19·88	19·84 19·92 19·87	19·88	±0·0	±0·0

The method is free from errors which occur normally when ammonia is titrated by alkalimetric methods. Traces of sodium hydroxide picked up by the vapour, dissolved alkali from the condenser or carbon dioxide dissolved from the air have no effect on the accuracy. Experience has shown that errors caused by traces of alkali picked up are only found if potassium hydroxide is used for liberating the ammonia. Another advantage of the method lies in the fact that only one standard solution is required. It is especially advantageous that the determination can be carried out even after an alkalimetric titration (see later).

DETERMINATION OF NITRATE IONS AFTER REDUCTION IN ALKALINE MEDIA

For the reduction of nitrate ions in alkaline media Devarda's alloy (50% Cu, 5% Zn and 45% Al) is usually recommended.[2] The method is simple and rapid, but a positive error occurs in almost all cases due to alkali picked up mechanically by the evolved hydrogen. The extent of the error depends largely on the construction of apparatus used; it can be reduced using an apparatus equipped with a trap,[9] but cannot be completely eliminated. The Schulek-Vastagh apparatus[10] is one of the best of this sort, but even using this an error of +3·8% in the determination of 30 mg sodium nitrate, due to the drops of alkali picked up by hydrogen, was found. Comparable experiments using a simple distillation apparatus (Fig. 1) which consisted of a 250-ml flask, a simple ball-condenser and a dropping funnel gave as much as +15% error. The error is a function of the quantity of Devarda's alloy used and of the velocity of hydrogen gas evolution. In addition there is frequently an error due to the alkali silicates dissolved from the condenser. Therefore even in the best constructed distillation apparatus a considerable positive error arises in the Devarda method, if the determination is finished by an alkalimetric titration of ammonia.

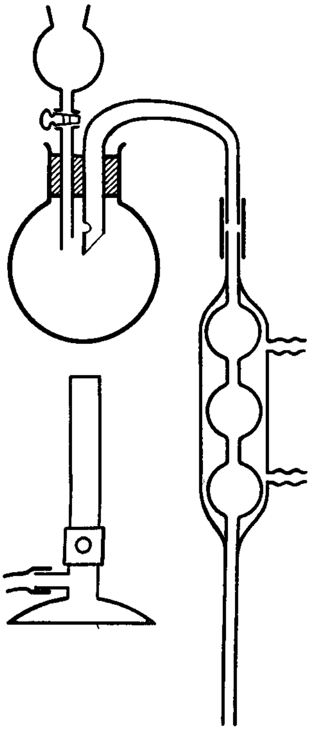

FIG. 1.

These errors can be eliminated if the ammonia is determined by precipitation of ammonia in form of ammonium tetraphenylboron instead of by an acid-base titration. The precipitate can be also weighed; but, especially when small amounts of ammonia are to be determined, it is more convenient to titrate it argentometrically. Since the determination is not sensitive to intrusive traces of alkali the simple apparatus of Fig. 1 may be used for the distillation. The use of potassium hydroxide must of course be avoided. The reduction and distillation time can be shortened to about 10 minutes, so that the total time required (which is lengthened by precipitation and filtration) is no greater than in the Devarda method. Na_2-EDTA should be used in the precipitation to complex the traces of the Devarda's alloy which occasionally pass through the apparatus. It is suggested that $0{\cdot}1N$ sulphuric acid should be used in the collector flask; its amount need not be known but it must always be in excess. For accurate work addition of methyl orange or methyl red to the sulphuric acid is not recommended since the end-point of the argentometric titration cannot readily be seen.

Experience has shown that using this simple distillation apparatus the determination can be carried out without error when 2–5-fold amounts of potassium, thallium, mercury or other heavy metal salts are present besides nitrate, since only negligible traces of these are carried over.

Procedure

The sample to be determined is weighed in the flask of the apparatus shown in Fig. 1. The sample which should contain 6–150 mg of nitrate is dissolved in 50 ml water and 2 g of well-powdered Devarda's alloy are added. The apparatus is assembled immediately, the collector flask containing 50 ml of $0{\cdot}1N$ sulphuric acid; 50 ml of 30% sodium hydroxide solution are added through the dropping funnel. The solution must be heated, first gently, but later more strongly, till 50 ml of liquid is distilled over. During this time the ammonia is distilled completely. When necessary, the acidity of the collector solution is checked using a small piece of litmus paper. On completing the distillation the cooler is lifted out of the collector flask and washed with water.

To the solution collected in the flask, 50 ml of $0{\cdot}2M$ sodium acetate and 50 ml of $0{\cdot}2M$ Na_2-EDTA solution are added the (pH of the solution is about 2–4), and after cooling $0{\cdot}1M$ sodium tetraphenylboron reagent is added dropwise until the latter is in slight excess. The mixture is allowed to stand for 15 minutes, and after this time the precipitate is collected on a thick filter paper (7 cm in diameter), and washed 5–6 times with the wash solution. The paper with the precipitate is returned to the flask in which the precipitation was carried out. The precipitate is dissolved in 15 ml of acetone by shaking, and 1–2 ml of $2M$ acetic acid and 1–2 drops of 1% Variamin Blue acetate indicator are added; the solution is then titrated with $0{\cdot}1N$ or $0{\cdot}01N$ silver nitrate solution until an intense blue colour appears. Near the end-point the silver nitrate is added dropwise and the mixture is mixed thoroughly after adding each drop. The solution should contain at least 50% of acetone at the end-point.

Sulphuric acid can be replaced by boric acid; 40 ml of saturated solution must be used and it is then unnecessary to use sodium acetate in the precipitation. Addition of Na_2-EDTA solution is of course necessary.

Comparative experiments were carried out using this alkaline reduction with (i) an acid-base, (ii) a tetraphenylboron-argentometric finish. The results are shown in Table II. Reduction and distillation were carried out in the Schulek-Vastagh apparatus in series I, and in the simple apparatus shown in Fig. 1 in series II. These results show that the tetraphenylboron method is accurate even when the simpler apparatus is used; on the other hand results obtained with acid-base titrations are inaccurate and deviations are high.

DETERMINATION OF NITRATE IONS AFTER A SULPHURIC ACID–SALICYLIC ACID DESTRUCTION

It is often necessary to determine nitrate ions in the presence of organic materials. In such case it is usual to form nitro compounds of aromatic substances which readily accept the nitro group. Such substances are, for example, salicylic acid or

TABLE II.—COMPARISON OF DISTILLATION APPARATUS

Dist. apparatus	0·1*N* $NaNO_3$,	0·1*N* HCl consumed after distillation,	Average,	Difference,		0·1*N* $AgNO_3$ consumed after distillation,	Average,	Difference,	
	ml	*ml*	*ml*	*ml*	%	*ml*	*ml*	*ml*	%
I	5·00	5·17 5·20 5·21	5·19	+0·19	+3·8	4·96 5·00 4·98	4·98	−0·02	−0·4
	20·00	20·34 20·20 20·28	20·27	+0·27	+1·35	20·01 20·02 20·02	20·02	+0·02	+0·1
II	5·00	5·75 5·60 5·82	5·72	+0·72	+14·4	4·95 4·99 5·03	4·99	−0·01	−0·2
	20·00	20·94 20·85 20·79	20·86	+0·86	+4·3	20·02 20·04 20·02	20·03	+0·03	+0·15

phenol. These nitro-compounds are easy to reduce in a concentrated sulphuric acid medium. After the reduction, organic material can be destructed by boiling with concentrated sulphuric acid.

Procedure

The organic material containing 10–120 mg nitrate is weighed on a cigarette paper strip, and added to a 250-ml Kjeldahl flask; 5–6 ml concentrated sulphuric acid containing 70 mg salicylic acid per ml are introduced. In the neck of the flask is placed a test-tube condenser. The mixture is heated carefully until dissolution is complete; the nitration of the salicylic acid is then also complete. 2–3 g of crystallized sodium thiosulphate are added and thoroughly mixed; finely divided elementary sulphur which precipitates reduces the nitro-group to the amino-group. After heating for 10–20 minutes the test-tube is removed from the neck of the flask, and, after addition of 0·05 g elementary selenium or 1 g copper sulphate as catalyst, destruction can be achieved by heating. If method (*a*) is used for the determination of the ammonia formed, selenium must be used as a catalyst. If the organic material is not destroyed easily, 2–3 g anhydrous solium sulphate must be added to the solution. After the destruction is complete (and the solution becomes clear) heating must be continued for about 20 minutes. Ammonia can be determined in this mixture by two different ways, (*a*) without distillation and (*b*) with distillation.

Method (*a*). The cold solution is diluted carefully (under cooling) with water up to 100 ml, 2 g sodium acetate are added and the solution is neutralized with 30% sodium hydroxide until thymol blue indicator changes from red to yellow. The pH of the solution is in this case between 2 and 4. After cooling, ammonium tetraphenylboron is precipitated with 0·1*M* sodium tetraphenylboron. The precipitate is filtered and washed, and is dissolved in acetone. After addition of 1–2 ml of 2*N* acetic acid the solution is titrated with 0·1*N* silver nitrate solution using Variamin Blue acetate indicator.

Method (*b*). The cold solution is diluted with water carefully to 100 ml, and is washed into the flask of a distillation apparatus. It is rendered alkaline with an adequate amount of 30% sodium hydroxide solution. The ammonia liberated is distilled into an excess of 0·1*N* sulphuric acid or 40 ml of saturated boric acid solution. The determination of ammonia can be carried out as described above.

According to results obtained in the determination of a sodium nitrate sample containing organic material, using both methods (*a*) and (*b*) the determination can be carried out with an average error of 0·3–0·7%.

Table III.—Analysis of chemical fertilizer "Pétisó"

Determination of ammonia-nitrogen content

Weight of the sample, mg	0·05N $AgNO_3$ consumed, *ml*	Nitrogen, %	0·1N HCl consumed, *ml*	Nitrogen, %	Difference from distillation method, *ml*	Difference from distillation method, %
140·15	19·45 19·40 19·37	9·70	9·74 9·71 9·76	9·74	−0·04	−0·4

Determination of total nitrogen content

Weight of the sample, mg	0·05N $AgNO_3$ consumed, *ml*	Nitrogen, %	0·1N HCl consumed, *ml*	Nitrogen, %	Difference from distillation method, *ml*	Difference from distillation method, %
140·15	39·20 38·92 39·06	19·53	19·50 19·45 19·40 19·46	19·46	+0·07	+0·3

DETERMINATION OF ORGANIC AZO, DIAZO AND NITRO COMPOUNDS

The nitrogen content of organic compounds cannot always be determined by the Kjeldahl method. If the nitrogen atom in the organic compound is not bound to carbon and hydrogen atoms, but there is a nitrogen–nitrogen or a nitrogen–oxygen bond, reliable results are obtained only when a reduction is first carried out. Sodium thiosulphate in a concentrated sulphuric acid medium gives good results for the reduction.

Procedure

The organic material containing 10–100 mg nitrogen is weighed on a cigarette paper strip, and added to a 250-ml Kjeldahl flask; 5 ml of concentrated sulphuric acid and 2 g of crystalline sodium thiosulphate are added. The mixture should stand for 12 hours. When the reduction is complete, organic material is destroyed and ammonia can be determined by either (*a*) or (*b*) as described above. Results obtained with this method are satisfactory for azobenzene, picric acid and dinitronaphthalene, and have an average error of 0·1–0·5%. Determinations on nitrobenzene and hydrazine sulphate were unsatisfactory.

PRACTICAL USES OF THE METHOD

The method has been used with satisfactory results for the determination of ammonium nitrogen and total nitrogen content of chemical fertilizers.

Procedure

7·005 g of the fertilizer was weighed into a 1-litre volumetric flask and water was added. The contents of the flask were shaken thoroughly and after sedimentation the mixture was filtered through a dry filter. The first part of the filtrate was discarded. 20·00 Ml of the filtrate were pipetted into a beaker and ammonia was precipitated with a slight excess of sodium tetraphenylboron (about 12–15 ml). After 15 minutes the precipitate was filtered and washed with a saturated solution of ammonium tetraphenylboron (it was found to be sufficient to wash it 5 times). The filter paper containing the precipitate was returned to the beaker in which the precipitation was made; the precipitate was dissolved in 15 ml acetone, 1–2 ml of 0·1*N* acetic acid and 1–2 drops of Variamin Blue acetate were added and the solution was titrated with 0·05*N* silver nitrate solution. The solution should contain at least 50% of acetone at the end-point.

To determine the total nitrogen content of the sample 20·00 ml of the filtrate were placed in a 100-ml Kjeldahl flask, and 0·5 g of *ferrum reductum*, 0·3 g of nickel sulphate and 15 ml of 2*N* sulphuric acid were added. The mixture was heated for 1 hour, when reduction was complete. After addition of 10 ml 2*N* sodium acetate the ammonium tetraphenylboron was precipitated by a slight excess (about 25–30 ml) of 0·1*M* sodium tetraphenylboron. The precipitate was filtered, washed, replaced in the Kjeldahl flask, and dissolved in 15 ml acetone. After addition of 1–2 ml of 0·1*N* acetic acid and 1–2 drops of Variamin Blue acetate indicator the solution was titrated to the appearance of the blue colour. The results obtained are shown in Table III.

Zusammenfassung—Eine neue Methode zur Bestimmung von Nitration wurde entwickelt. (*a*) Nitrat wird in saurem Medium durch Eisen(II)—sulfate in Gegenwart von Nickelsulfate zu Ammoniak reduziert. Ammoniak kann aus saurem Medium mit Tetraphenylbor gefällt werden. Nach Filtrieren und waschen wird der Niederschlag in Azeton gelöst und das Tetraphenylbor mit Silbernitrat titriert, wobei Variamin Blau-acetat als Indikator dient. (*b*) Nitrat wird in alkalischer Lösung nach Dewarda reduziert, das Ammoniak abdestilliert und nach der obigen Methode bestimmt. Die neue Methode wurde zur Bestimmung von Nitrat in Gegenwart von organischen Substanzen verwendet, sowie zur Bestimmung von Nitroso-, Azo und Diazoverbindungen.

Résumé—On propose une nouvelle méthode pour le dosage du nitrate: (*a*) Les ions nitrate peuvent être réduits en ammoniaque par réduction en milieu acide par l'ion ferreux en présence de sulfate de nickel. L'ammoniaque peut être précipité en milieu acide à l'état de tetraphénylborure d'ammonium. Après filtration et lavage, le précipité peut être dissous dans l'acétone et la solution peut être titrée par le nitrate d'argent en utilisant l'acétate de bleu de variamine comme indicateur. (*b*) Les ions nitrate peuvent être réduits en milieu alcalin par la méthode de Devarda, l'ammoniaque étant alors distillé et titré comme précédemment. Cette nouvelle méthode a été appliquée au dosage de nitrates en présence de matières organiques et au dosage de composés nitrosés, azoiques et diazoiques.

REFERENCES

[1] K. Ulsch, *Angew. Chem.*, 1891, **4,** 241; *Z. analyt. Chem.*, 1891, **30,** 175.
[2] A. Devarda, *Chem.-Ztg.*, 1892, **16,** 1952.
[3] Th. Arnd, *Angew. Chem.*, 1917, **30,** 169; 1920, **33,** 296; 1932, **45,** 22, 745.
[4] T. Teorell, *Acta Med. Scand.*, 1928, **68,** 305.
[5] Z. Szabó and L. G. Barta, *Analyt. Chim. Acta*, 1951, **5,** 33.
[6] Z. Szabó, L. G. Barta and F. Simon-Fiala, *Acta Chim. Acad. Sci. Hung.*, 1953, **3,** 231.
[7] L. Erdey, K. Vigh and L. Pólos, *Talanta*, 1959, **3,** 1.
[8] N. Martin, *J. prakt. Chem.*, 1854, **61,** I. 247.
[9] R. Kieselbach, *Analyt. Chem.*, 1944, **16,** 765.
[10] E. Schulek and G. Vastagh, *Z. analyt. Chem.*, 1923, **92,** 352.

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A DIRECT-READING CURRENT INTEGRATOR FOR COULOMETRIC ANALYSIS

SHIGEKI HANAMURA
Government Industrial Research Institute, Nagoya, Japan

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Summary—A direct reading current integrator for coulometric analysis has been developed. This employs a bevel gear differential and a standardization device incorporated to add stability to the instrument as a whole. The advantages over existing coulometers and integrators include a high power output, a stable curve through the origin, the integration of small currents, no dead zone, and a cancellation of the background current by a zero adjustor. Under good conditions about 0·3% deviation may be achieved. The determination of copper by controlled potential shows that this instrument is applicable to coulometric analysis.

COULOMETRIC analysis with controlled potential and with constant current techniques requires the accurate measurement of the quantity of electricity passed through the electrolysis cell. In the constant current technique, this may be measured by counting the current and the time, by using chemical coulometers (*i.e.* the silver, titration, hydrogen-oxygen, or hydrogen-nitrogen coulometers),[1] or by using electromechanical integrators, such as the low-inertia integrating motor.[2] In the controlled potential technique, this also may be measured by using any chemical coulometer or any integrator (*i.e.* Lingane-Jones' ball and disc integrator,[3] Meites' electromechanical integrator,[4] or others[5]), or by integrating the current-time curve.[6] Although very precise, chemical coulometers are inconvenient and require much manipulation.

At present there are various types of integration methods, one of which is the commutator motor type. The principle of this type is based on the fact that the rotor revolution speed n at any one moment is proportional to the input current i:

$$n \propto i$$

or, when converted to an equation:

$$n = \mathrm{K}i$$

Upon integration from t_1 to t_2, the following equation is derived:

$$\int_{t_1}^{t_2} n\, dt = \mathrm{K} \int_{t_1}^{t_2} i\, dt$$

The quantity of electricity Q corresponds to $\mathrm{K}\int_{t_1}^{t_2} i\, dt$, and also, $\int_{t_1}^{t_2} n\, dt$ equals the total number of revolutions. Therefore, the quantity of electricity corresponds to the sum total of revolutions.

The integrator using a low-inertia integrating motor is based on this principle. In this motor, as in all mechanical devices, mechanical friction is always present. It influences the dead zone (starting voltage is always required) and also makes it difficult to integrate increasing current from small current in the neighbourhood of zero. These influence the stability and the linearity of the rotating speed versus the input current. Thus when the integrator is designed to decrease this friction, the over-all output power is cut down, resulting in difficulty when using a large-scale counter. An integrator so designed is sensitive to external conditions such as temperature, so that it is difficult to keep the linearity constant. To eliminate such disadvantages, the present author has used a bevel gear differential and various motors and has obtained good results.

This paper describes a current integrator which is readily adaptable to both the constant current and the controlled potential techniques. The bevel gear differential is the main mechanism, and is driven by a d.c. integrating motor. When this integrator is used with the constant current apparatus, the timer is eliminated and a simple current source is usable, *i.e.* a battery and a high resistor; with the controlled potential apparatus, chemical coulometers are unnecessary. Further advantages for both techniques are that this device possesses a high power output which can be adapted to drive other mechanisms, such as recorders and/or large-scale mechanical counters; it draws a characteristic curve which is linear and passes through the origin; it makes direct reading possible; it eliminates the dead zone; it permits small current integration in the neighbourhood of zero per cent of rated current, *i.e.* rated current of the lowest range—1 mA. Table I shows the relation of count/coulomb versus input current at a rated current of 50 mA. The range below 2% of rated current has not been measured; however, measurement of the observed current between 2% and zero is possible, although with a rather large deviation. Using the constant current technique with this integrator, about 0·3% coefficient of variation may be obtained by selecting the input sensitivity range which provides a suitable current between 50 to 100% of rated current. Using the controlled potential technique, about 0·39% coefficient of variation may be obtained by selecting the input sensitivity range which provides an initial electrolysis current near the rated current. Table I indicates that at lower per cents of rated current, the deviation is large; however, this has little effect on the practical determination, for there is a possibility of obtaining a coefficient of variation about 0·39% (Table II).

TABLE I.—CALIBRATION FACTORS
(count/coulomb)

I(mA)	1	3	5	10	20	30	40	50
$\bar{x}$	388·8	383·0	383·4	382·6	381·7	382·9	381·6	381·6
Std. dev.	16·97	4·74	1·89	1·51	0·89	1·32	0·93	0·77
C.V. (%)	4·36	1·24	0·49	0·39	0·23	0·34	0·24	0·20

I : input current
$\bar{x}$: mean count/coulomb of 10 measurements
Std. dev.: standard deviation
C.V. : $\frac{\text{Std. dev.}}{\bar{x}}$ = coefficient of variation

TABLE II.—ESTIMATED DEVIATION FOR CONTROLLED POTENTIAL COULOMETRIC ANALYSIS·

Q_i	C.V.	Dev. = $Q_i \times$ C.V.
$Q \times [(50 - 40)/50]$	0·002	0·0004 · Q
$Q \times [(40 - 30)/50]$	0·0024	0·00048 · Q
$Q \times [(30 - 20)/50]$	0·0034	0·00068 · Q
$Q \times [(20 - 10)/50]$	0·0023	0·00046 · Q
$Q \times [(10 - 5)/50]$	0·0039	0·00039 · Q
$Q \times [(5 - 3)/50]$	0·0049	0·000196 · Q
$Q \times [(3 - 1)/50]$	0·0124	0·000496 · Q
$Q \times [(1 - 0)/50]$	0·0436	0·000872 · Q
		/+
Q	total C.V.	0·003974 · Q

therefore, the deviation for the total quantity of electricity is 0·39%.

Q: total quantity of electricity.

Q_i*: quantity of electricity which is assumed to be measured with coefficient of variation at each input current value.

C.V.: coefficient of variation from Table I.

Dev.: deviation at each Q_i.

* With controlled potential technique

$$i_t = i_0 \, 10^{-Kt} \qquad (1)[1]$$

$$Q = \int_0^t i_t \, dt \qquad (2)$$

from equations (1) and (2)

$$Q \fallingdotseq \frac{i_0 - i_t}{2{\cdot}303K} \qquad (3)[10]$$

therefore, i_t and Q are proportional.

APPARATUS

This integrator (Fig. 1) consists essentially of the following units: 1. an integrating motor driving unit: a d.c. motor and d.c. motor control unit; 2. an error detection and correction unit: a 2-phase servo motor, a.c. amplifier, and d.c. tachogenerator; 3. a d.c. supply source; 4. a bevel gear differential; 5. a synchronous motor; 6. a counter.

Bevel gear differential[7]

The differential gear (Fig. 2) is composed of 1. a vertical shaft Y–Y′ and a horizontal shaft X–X′ which are fixed; 2. bevel gears which are free on the two shafts. A constant input gear speed is supplied by a synchronous motor; a variable input gear speed, dependent on the measuring current, is provided by a d.c. integrating motor.

When the two gears A and A′ revolve reversely and at the same speed, the gears B and B′ on the horizontal shaft also revolve equally. The fixed shafts are stationary and register a zero reading. When gear A revolves faster than gear A′, the revolutions of the gears B and B′ alone are not capable of equalizing this increased speed of gear A. To accommodate this increase, the X–X′ shaft rotates about the Y–Y′ shaft in the same direction as the faster gear A is revolving. The X–X′ shaft rotates about the Y–Y′ shaft according to the equation

$$S_{Y-Y'} = \frac{S_A - S_{A'}}{2}$$

where S_A is the speed of the integrating motor, $S_{A'}$ is the speed of the synchronous motor (always constant), and $S_{Y-Y'}$ is the rotation speed of the Y–Y′ shaft. This speed of the Y–Y′ shaft is proportional to the measuring current, because the quantity of electricity corresponds to the total number of revolutions.

Brass bevel gears with 24 teeth and a diameter of 18·5 mm are used for the differential gear. The input gears from the synchronous motor and the integrating motor are of the same type.

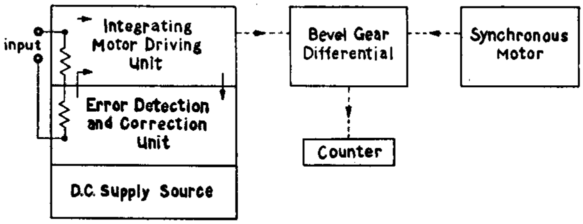

FIG. 1.

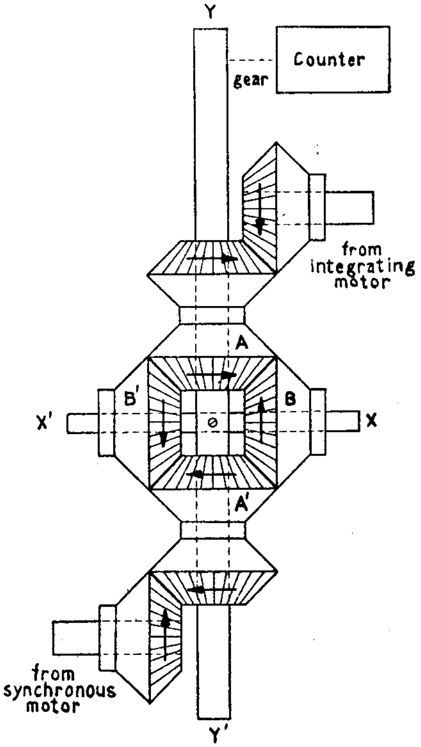

FIG. 2.

Integrating motor driving unit

The d.c. motor of the driving unit is a micromotor with a tachogenerator which are built in one body and have a common shaft. The micromotor, Model CLE 3R-60 of Nihon Micromotors Co., has characteristics (rated values) of 7·5 V input voltage, 92 mA maximum current, and 0·75 watt. This motor follows the 12 cycle square wave input current (*i.e.* the direction of rotation changes 24 times per second).

The plate current of a 6Y6 vacuum tube controls this micromotor (Fig. 3). The observed current is added to the input grid resistor. The 4 kilo-ohm input resistor gives a rated current of 1 mA, and if necessary the rated current may be adjusted by replacing the input resistor or by using a shunt resistor. This induced grid voltage of 6Y6 varies, in turn proportionally altering the plate current.

Therefore, this plate current affects the d.c. integrating motor speed. If necessary the cathode resistor R_3 (ordinary variable resistor) of the 6Y6 tube controls the motor speed. When the amplified error voltage drives the 2-phase servo motor, a worm gear train transfers the rotation to the above-mentioned variable resistor R_3.

Error detection and correction unit

As stated above, the proportional relation of the observed current and the integrating d.c. motor speed is not always constant. To keep this relation constant, this integrator requires an error detection and correction unit. For such a correction, a standard is necessary. The linear and relatively stable characteristic curve of output voltage versus tachogenerator speed provides this standard.

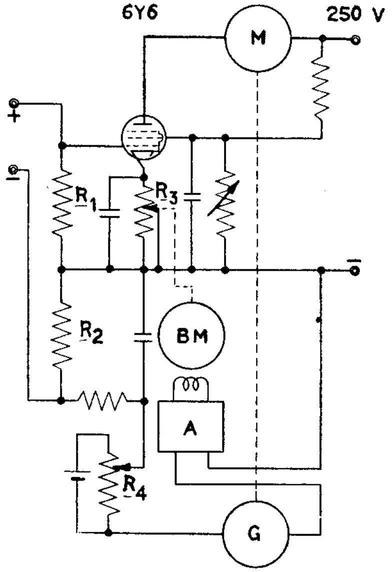

FIG. 3.

The observed current moves the d.c. motor. The voltage of the generator is proportional to the d.c. motor speed (generator and motor being on one shaft). The observed current also induces the voltage of the input standard resistor (R_2 in Fig. 3). If a difference occurs between the generated voltage and the induced voltage, this voltage difference is amplified by the a.c. amplifier and drives the 2-phase servo motor. This motor in turn controls the d.c. motor speed by the cathode of the 6Y6 tube until the generator voltage equals the input standard resistor R_2 voltage. Therefore the proportional relation of the d.c. motor speed and the observed current becomes constant.

When the observed current is zero, the cathode resistance and screen grid voltage adjust the initial d.c. motor speed to equal the synchronous motor speed (differential gear shafts are stationary). The voltage of the generator, proportional to the d.c. motor speed, is cancelled by voltage from a dry cell and a variable resistor R_4. When the dry cell voltage is changed, a difference occurs between the generator voltage and the altered dry cell voltage. This difference is amplified in the error detection unit, and in turn changes the d.c. motor speed. The zero adjustment of the counter is controlled by this variable resistor R_4. The dry cell voltage is always superimposed on the observed current voltage.

The a.c. amplifier of the error detection unit consists of an a.c. converter and two 12AX7 and one 6AU7 vacuum tube. The detected error voltage is converted to 60-cycle alternating current, is amplified to about 100 dB by the tubes 12AX7 and 6AU7, and is used to drive the 2-phase servo motor.

The tachogenerator, Model CLE 3R-60, has a speed of 30 to 48 r.p.m. (gear ratio 1 : 60) and an output of 6 mV per 1 r.p.m. This tachogenerator was used because the characteristic curve is linear in the range that was used.

d.c. supply source

A rectifier tube 80BK and an ordinary radio-use power transformer are used for the d.c. supply source. The output d.c. voltage is 250 volts; the rated current is 65 mA.

Synchronous motor

A 5 watt, 30 r.p.m. synchronous motor is used.

Counter

A needle-type, 5-unit counter (meter type) is used, because the driving power of digital-type counters is not constant (more power required every 10 units). The driving power of this needle-type counter is supplied by the output and is always constant.

To summarize: The observed current drives the d.c. integrating motor, which in turn drives one input of the differential gear. At the same time the synchronous motor drives the other input of the differential gear. The difference between the speed of the two motors is indicated by the counter. The count equals the total number of revolutions, which in turn equals the quantity of electricity. The stability is kept constant by the d.c. tachogenerator of the error detection unit.

Although this is a complicated mechanism, this apparatus is easily assembled in an ordinary laboratory, since all the gears rotate in only one direction. This enables the use of mechanical parts which need not be of highest quality; the total character of the apparatus, however, is not affected.

The typical calibration factors, obtained over several days, are shown in Table I. The input current used was rated at 50 mA (input resistor about 100 ohms). The standard quantity of electricity was calculated from the constant current and time. The count per coulomb was calculated from the standard number of coulombs and from the count at the various current values. With the constant current technique, the smallest deviation is obtained in the range of 50 to 100% of the rated current. With the controlled potential technique, the initial deviation is small—about 0·2%, since the initial electrolysis current is adjusted (at the input section) to the neighbourhood of 100% of the rated current; but as the electrolysis current decreases to the lower 10% of the rated current, the deviation becomes larger—about 4%. However, the total deviation is small—about 0·39% (Table II), when the entire range from 0 to 100% of the rated current is taken into consideration. These results only show the range from 2 to 100% of rated current; however, it is possible to measure the input current in the neighbourhood of zero, although with some loss in accuracy.

EXPERIMENTAL

The determination of copper was carried out to test the applicability of this integrator to controlled potential coulometric analysis. Copper sulphate solutions containing from 0·5 to 5·0 mg copper and 0·5*N* hydrochloric acid were used. The cathode was a copper-gauze cylinder. The method of determination, described by Yamashita and the present author in a previous publication,[8] has been modified slightly in this experiment.

Cell

The cell used is shown in Fig. 4. The cathode chamber has a volume of 200 ml; the anode chamber 80 ml; and the middle chamber 30 ml. Between these chambers are sintered-glass discs of 20-mm diameter.

Electrodes

The cathode is a 25-mesh copper-gauze cylinder with a diameter of 30 mm and a height of 30 mm. The anode is a 1-mm platinum spiral wire. The saturated calomel electrode is one of the commercial portable type.

Reagents

99·99% copper was used for the standard sample. Copper sulphate solutions were made from the standard sample with concentrations of 0·462 mg per 10 ml, $0{\cdot}924_5$ mg per 10 ml, $2{\cdot}311_5$ mg per 5 ml, and 4·623 mg per 10 ml. The electrolyte was 0·5*N* hydrochloric acid (reagent grade).

Automatic potential control

This unit employs a modified Lingane-Jones' potentiostat[9] which is on the market in Japan.

Procedure

The cathode chamber is filled with 100 ml of hydrochloric acid, the anode chamber with 60 ml, and the middle chamber with 25 ml (the middle chamber acid level is higher than others). The electrodes are set up and connected as shown in Fig. 4. The cathode potential of the potentiostat is adjusted to $-0{\cdot}34$ V versus S.C.E. A magnetic stirrer continually agitates the cathode chamber. A rapid stream of nitrogen gas, initially passed through pyrogallol solution for removal of oxygen, is used throughout the determination. Nitrogen gas is bubbled through the cathode chamber for 15 min before pre-electrolyzing. Pre-electrolyzing is continued till the background current becomes very nearly constant. Even at this point there is a slight trace of dissolved copper and other unreducible impurities. Although this trace is constantly present, it has no effect on the results. When the background current becomes nearly constant, the counter reading is set at zero by adjusting the variable resistor R_4 (zero adjustor) to change the d.c. motor speed to equal the synchronous motor speed. A known volume of the sample is then pipetted into the cell, and the electrolysis is continued until the counter comes to a stop. At this point the background current has again become nearly constant. This counter reading is the net quantity of electricity consumed for the electrolysis of copper to be determined: *i.e.* the total quantity of electricity passed through the cell minus the quantity of electricity required by the background current. The number of coulombs is calculated from this counter reading and a factor (count/coulomb). The copper content can be calculated from this number of coulombs.

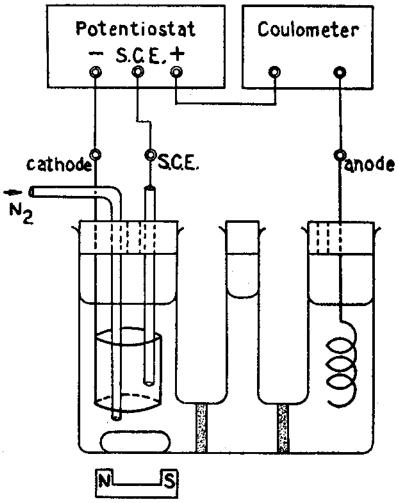

FIG. 4.

RESULTS

A cross-section of results obtained in the determination of various quantities of copper is shown in Table III. The electrolyses required about 10–15 minutes after each sample was introduced. The coefficient of variation of the 0·462-mg sample is larger than the coefficient of variation of the other samples. The initial concentration of the 0·462-mg sample is of the order of $10^{-4}M$, so that this difference in coefficients of variation may be large; consideration shows, however, that the standard deviation of the 0·462-mg sample has about the same value as that obtained from the other samples. The differences between the theoretical concentrations and the means of the

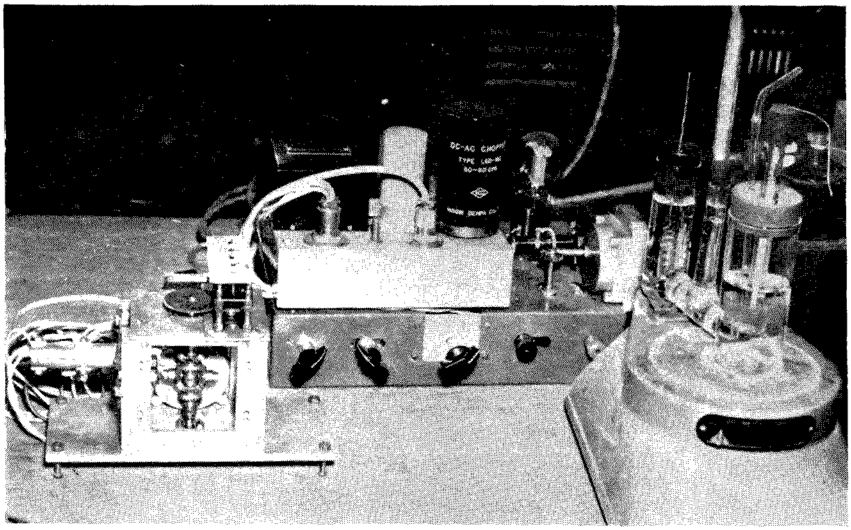

FIG. 5.

measured concentrations are all negative values. This seems to be due to systematic error; the cause has not been ascertained. Error may possibly be introduced into the calibration factor by the fluctuation of constant current source and by error in time and current measurement. The use of a silver coulometer to obtain the calibration factor might yield better accuracy.

TABLE III.—COULOMETRIC DETERMINATION OF COPPER

Taken, *mg*	Equiv. to, *coul*	Found, *coul*	Mean, *coul*	Std. dev., *coul*	Std. dev., *mg*	C.V., %	Diff., *mg*
0·462	1·404	1·303 1·329 1·337 1·379 1·426 1·457	1·372	0·055	0·018	4	−0·011
0·925	2·807	2·658 2·697 2·681 2·653 2·692	2·676	0·019	0·006	0·7	−0·043
2·312	7·019	7·029 7·052 6·932 6·971 7·089	7·015	0·056	0·018	0·8	−0·001
4·623	14·039	13·995 13·930 13·896 14·039 14·039 14·112	14·002	0·072	0·024	0·5	−0·012

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Zusammenfassung—Ein direkt anzeigender Stromintegrator für coulometrische Analysen wurde entwickelt. Das Instrument enthält ein konische Differential-Verzahnung und eine Standardisierungsvorrichtung was zur Stabilisierung der gesamten Anordnung beiträgt. Der Vorteil gegenüber bestehenden Instrumenten liegt u.a. in folgendem: hohe Energieleistung, stabile Kurve durch den Ursprung, Integration auch kleiner Ströme, Fehlen einer "Leerzone" und Vorhandensein eines Nullpunktkompensators. Bei guten Bedingungen werden Abweichungen von nur 0,3% erhalten. Die Bestimmung von Kupfer zeigte die Anwendbarkeit des Instrumentes in coulometrischen Analysen.

Résumé—L'auteur propose un intégrateur de courant à lecture directe pour l'analyse coulométrique. Celui-ci utilise un engrenage conique différentiel et un dispositif d'étalonnage incorporé pour augmenter la stabilité de l'instrument.

Les avantages sur les coulomètres et intégrateurs existants sont: une grande puissance de sortie, une courbe stable jusqu'à l'origine, l'intégration de petits courants, l'absence de zone morte, et l'élimination du courant résiduel par un réglage de zéro. Dans de bonnes conditions on peut atteindre un écart de 0,3 %. Le dosage du cuivre à potentiel contrôlé montre que cet appareil est utilisable en analyse coulométrique.

REFERENCES

[1] J. J. Lingane, *Electroanalytical Chemistry*, Interscience Publishers, New York, 2nd Ed., 1958.
[2] J. S. Parsons, W. Seaman, and R. M. Amick, *Analyt. Chem.*, 1955, **27**, 1754.
[3] J. J. Lingane and S. L. Jones, *ibid.*, 1950, **22**, 1220.
[4] L. Meites, *ibid.*, 1955, **27**, 1116.
[5] I. A. D. Lewis and B. Collinge, *Rev. Sci. Instrum.*, 1953, **24**, 1113.
[6] W. MacNevin and B. B. Baker, *Analyt. Chem.*, 1952, **24**, 6.
[7] G. W. Michalec, *Machine Design*, 1955, 178–188.
[8] M. Yamashita and S. Hanamura, *Reports of the Government Industrial Research Institute, Nagoya*, 1957, **6**, 635. (in Japanese).
[9] J. J. Lingane and S. L. Jones, *Analyt. Chem.*, 1950, **22**, 1169.
[10] S. Hanamura and M. Yamashita, *Reports of the Government Industrial Research Institute, Nagoya*, 1957, **6**, 723. (in Japanese).

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CONTRIBUTIONS TO THE CHEMISTRY OF SELENIUM AND SELENIUM COMPOUNDS—II

THE IODOMETRIC DETERMINATION OF SELENOCYANIDE*

E. SCHULEK and L. BARCZA
Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary

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Summary—The interference of certain anions in the iodometric determination of selenocyanide has been examined. Sulphate, chloride and perchlorate do not interfere, whilst in the presence of bromide, selenocyanide can only be partially oxidised by bromine to selenite, so that high results are obtained. The interference of bromide can be eliminated by sodium tungstate, or by determining the bromocyanogen formed, after distillation.

IN a preceding communication,[1] a method was presented for the micro determination of elementary and loosely bound selenium. Other micromethods for the determination of selenium and selenium compounds were also discussed in detail.

As we desired to apply this method in a rather broad field to the analysis of selenium and its compounds, the possibilities of determination in the presence of various anions were first subjected to a thorough examination.

It was found that selenium can be determined with an adequate accuracy even in the presence of large amounts of chloride, sulphate and perchlorate, although in the case of extremely high concentrations of sulphate a stronger acidification of the solution is necessary. Bromide ions interfere in relatively low concentrations.

In practice, the presence of bromide ions must always be taken into account. The interpretation of its interference and the possibilities of its elimination will therefore be discussed here in detail.

On brominating selenocyanide under prescribed experimental conditions (concentration, pH, temperature),[1] a reaction characterised by the following overall equation takes place:

$$SeCN^- + 4Br_2 + 4H_2O = BrCN + SeO_4^{2-} + 7Br^- + 8H^+ \qquad (1)$$

It must be emphasized, however, that in the course of bromination several processes which reach equilibrium with each other must be considered.

The amount of excess bromine added was found to play an essential role in the determination. When only as much bromine-water is added to the solution as is required to obtain a slightly yellow colour, after binding the bromine with phenol, selenite can still be detected in the solution, in addition to bromocyanogen and selenate. This proves that, of the reactions combined into the overall equation (1), the oxidation of selenite leads mainly to the equilibrium:

$$H_2SeO_3 + Br_2 + H_2O \rightleftharpoons HSeO_4^- + 3H^+ + 2Br^- \qquad (2)$$

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* Paper I of this series: *Z. analyt. Chem.* 1953, **139**, 20.

According to the measurements of Sherril and Izard,[2] the equilibrium constant of this reaction is of the order of 0·88. Thus, the reaction in the forward direction can only be complete at a low concentration of hydrogen and bromide ions. By increasing in favour of the quantity of bromide ions, reaction (2) shifts the formation of selenite.*

In an acid medium selenite oxidizes iodide to iodine with liberation of elementary selenium; in a bicarbonate medium selenite is not oxidised to selenate by iodine.[3]

This simple interpretation of the interfering effect of bromide suggested the necessity for a modification of the method when higher concentrations of bromide ion are present. The interference may be eliminated either by reducing the concentration of selenate (effectively of selenite) or by removing the bromocyanogen. When the solution contains bromide ions, selenate cannot be precipitated by barium ion, due to the solubility of barium selenate in acid media. In contrast, good results were obtained even at much higher concentrations of bromide, when sodium tungstate was added to the reaction mixture. Sodium tungstate presumably forms an extremely stable heteropolyacid, poorly reducible by haloids.† However, at the same time care must be taken to maintain a low concentration of hydrogen and iodide ions.

THE TUNGSTATE METHOD

Reagents

All the reagents should be of analytical grade.
Perchloric acid, 10% solution.
Methyl red, 0·1% ethanolic solution.
Sodium tungstate.
Bromine-water, freshly prepared, saturated.
Phenol, 5% solution.
Sodium thiosulphate, 0·01*N* solution, preserved by 1% of *iso*butanol.
Starch, 1% solution of potato starch (decomposed) preserved with 0·1% salicylic acid.
Potassium iodide.

A solution of selenocyanide corresponding to 0·4–4·0 mg of selenium is prepared by weighing accurately and diluted to 40–45 ml. It is transferred into a 100-ml Erlenmeyer flask fitted with a glass stopper, and is neutralised in the presence of methyl red. (When bromide is present, 0·2 g of sodium tungstate should be dissolved in the reaction mixture before neutralisation). The neutral solution is treated with bromine-water until it turns definitely brownish yellow and is allowed to stand for 2–3 minutes; 2–4 ml of phenol solution are added and the contents are allowed to stand for 4–5 minutes and acidified with 2 ml of perchloric acid. After adding 0·1–0·2 g of potassium iodide to the solution and allowing it to stand for 20 minutes, the amount of liberated iodine is measured. When a large amount of sulphate is present, 5 ml of perchloric acid should be added.

1 ml of 0·01*N* $Na_2S_2O_3$ is equivalent to 0·3948 mg of Se.

The effect of tungstate will be dealt with in a subsequent communication.

It was also found to be possible to determine selenocyanide in the presence of bromide by distilling the bromocyanogen formed. This method offers the advantage that the solution can be subjected also to other investigations, after the determination of selenocyanide.

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* It is of interest to note that the equilibrium constant of the reaction selenite-chlorine is recorded as $1·4 . 10^9$.

† This possibility was suggested by E. Pungor.

TABLE 1

Quantity of Se weighed as KSeCN, *mg*	Foreign substances	0·01*N* $Na_2S_2O_3$ consumed, *mg*	Se found, *mg*	Deviation %	Notes
1·961	0·85 g K_2SO_4	4·97 4·96	1·962 1·958	+0·1 −0·2	— —
	4·2 g K_2SO_4	4·94 4·96	1·950 1·958	−0·6 −0·2	Stronger acidification
	0·75 g KCl	4·96 4·97	1·958 1·962	−0·2 +0·1	— —
	1·4 g $NaClO_4$	4·97 4·97	1·962 1·962	+0·1 +0·1	— —
	0·3 g KBr	7·5 6·9	2·90 2·67	+48 +36	— —
	0·1 g KBr	6·5 5·7	2·45 2·20	+25 +12	— —
		6·0 6·5	2·32 2·45	+18 +25	0·25 g $BaCl_2$
	0·15 g KBr	4·97 4·96	1·962 1·958	+0·1 −0·2	0·20 g Na_2WO_4
	0·3 g KBr	4·96 4·95	1·958 1·954	−0·2 −0·4	
	0·6 g KBr	4·95 4·96	1·954 1·958	−0·4 −0·2	
	0·15 g KBr	4·97 4·96	1·962 1·958	+0·1 −0·2	BrCN removed by distillation
	0·3 g KBr	4·98 4·97	1·966 1·962	+0·3 +0·1	
	0·6 g KBr	4·97 4·97	1·962 1·962	+0·1 +0·1	

THE DISTILLATION METHOD

Reagents

With the exception of sodium tungstate, the reagents are as used in the tungstate method. In addition a concentrated solution of phosphoric acid (80%) is required.

A solution of selenocyanide corresponding to 0·4–4·0 mg of selenium, accurately weighed, is neutralised in the presence of methyl red in a 100-ml round bottomed flask[4] fitted with a glass condenser connected with a ground glass joint. Excess bromine-water is added. Some glass beads are put in the distilling flask, the joints are lubricated with concentrated phosphoric acid and the flask is connected with the condenser. A 100-ml glass-stoppered Erlenmeyer flask containing 30 ml of water or preferably a 100-ml glass-stoppered measuring flask with a neck narrowed at one point[5] serves as receiver. The tube of the condenser touches the bottom of the receiver flask. The reaction mixture is heated by a small flame, using efficient condensing, and distillation is continued for 4–5 minutes. The tube of condenser is then raised to 1–2 cm above the distillate, and distillation is continued for further 1–2 minutes, in order to wash the condenser. Now the distillate, which contains bromine in addition to bromocyanogen, is treated with 2–4 ml of phenol solution and allowed to stand for 5 minutes; 2 ml of perchloric acid and about 0·1 g of potassium iodide are added. After allowing the liquid to stand for 20 minutes, the amount of liberated iodine is measured with a 0·01*N* solution of sodium thiosulphate.

1 ml of 0·01*N* $Na_2S_2O_3$ solution is equivalent to 0·3948 mg of Se.

The results obtained are shown in Table I.

Zusammenfassung—Das früher angegebene Verfahren zur Bestimmung von Selen über Selenocyanid wurde bezüglich störender Wirkung von Anionen gründlich untersucht. Sulfate, Chloride, Perchlorate übten keinen störenden Einfluss auf die Bestimmung aus. In Gegenwart von Bromiden konnte die störende Einwirkung durch Hinzugabe von Komplexbildner, wie das Natriumwolframat behoben werden. Sehr gute Resultate konnten durch das Abdestillieren des zur jodometrische Bestimmung gelangenden BrCN erzielt werden.

Résumé—Les auteurs ont étudié l'influence gênante de certains anions dans le dosage iodométrique du sélénocyanure. Les sulfates, chlorures et perchlorates ne faussent pas les résultats mais en présence de bromure le sélénocyanure est oxydé seulement partiellement par le brome en sélénite. Dans ce dernier cas les résultats sont donc trop élevés. On peut cependant éliminer l'action gênante des bromures par le tungstate de sodium ou en déterminant, après distillation, le bromure de cyanogène formé.

REFERENCES

[1] E. Schulek and E. Körös, *Z. analyt. Chem.* 1953 **139,** 20.
[2] M. S. Sherril and E. F. Izard *J. Amer. Chem. Soc.* 1928 **50,** 1665.
[3] H. Schulze, *J. prakt. Chem.* 1885, (2) **32,** 400.
[4] E. Schulek and G. Vastagh, *Z. analyt. Chem.* 1931 **84,** 167.
[5] E. Schulek, K. Burger and M. Fehér, *Z. analyt. Chem.*, 1959, **167,** 723.

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CONTRIBUTIONS TO THE CHEMISTRY OF SELENIUM AND SELENIUM COMPOUNDS—III

MICRODETERMINATION OF SELENITE THROUGH BROMOCYANOGEN

E. SCHULEK and L. BARCZA
Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary

(*Received* 20 *March* 1959)

Summary—At a suitable pH selenite can be reduced by ascorbic acid. On converting it into selenocyanide it is possible to determine it precisely on the micro scale by iodometry. The excess of reductant is eliminated by bromine, and the interference of the bromide formed is eliminated by tungstate or by distillation.

IN earlier communications, the iodimetric microdetermination of elementary selenium through selenocyanide was dealt with in detail. By this method, it is possible to determine other selenium compounds as well, since these can relatively easily be converted into elementary selenium.

Quadrivalent selenium in selenium dioxide can be converted into elementary selenium by repeated evaporations with hydrazine hydrate and it is possible to remove the excess of the reducing agent in a simple way.[1] When other substances such as acids or bases are present in addition to selenium dioxide, the excess of reducing agent cannot be removed by simple evaporation alone. Attempts to eliminate excess reducing agent by raising the amount of bromine used for the bromination of selenocyanide resulted in an appreciable increase of the concentration of bromine in the solution.

A method for the elimination of interference from bromide has already been described.[2] On the basis of our experiments, the problem may be solved in another way after consideration of the following points:

(1) reducing quadrivalent selenium satisfactorily,
(2) adjusting the pH value, after reduction, to an adequate degree,
(3) dissolving the reduced elementary selenium, and
(4) removing excess cyanide.

These problems are interconnected. The adjustment of pH is difficult. Selenite can only be reduced to elementary selenium in an acid medium, but higher pH values would be desirable to facilitate the dissolving of elementary selenium in potassium cyanide. The simplest method is to adjust the solution before reduction, in the presence of methyl red, to give a neutral or acid reaction, and to make the solution alkaline after reduction, in the presence of sufficient potassium cyanide to dissolve the precipitated selenium. The pH value not exceeding 8 required for the elimination of cyanide by boiling, is secured by the addition of boric acid.

A reducing agent is therefore required which is capable of reducing selenite quantitatively at a pH value of about 5. Hydrazine sulphate or ascorbic acid meet this requirement. It is desirable that excess reducing agent should instantaneously be oxidized by bromine, and that in the course of the bromination only products which do not react with iodide or iodine should form. In some cases hydrazine sulphate was observed to interfere so that only ascorbic acid proved suitable.

At a pH value of about 5, selenite is not instantaneously reduced by ascorbic acid, and if the reaction is hastened by heating, selenium is converted into its crystalline modification which is insoluble in a solution of potassium cyanide.* At room temperature reduction proves to be complete in 10 minutes when 50 mg of ascorbic acid are added to 10 ml of solution.

The colloidal selenium formed during reduction in the cold dissolves in a solution of potassium cyanide in a few seconds, and with the concentration examined 50 mg of potassium cyanide are satisfactory for this purpose. Larger quantities of cyanide are only needed when the solution remains slightly acidic before reduction.

On diluting the solution, excess cyanide can easily be removed by boiling the solution with boric acid.

The selenocyanide content of the resulting solution can be determined by the tungstate or the distillation methods previously described.

THE TUNGSTATE METHOD

Reagents

In addition to the reagents listed previously for the tungstate method[2], the following are necessary:

Sodium hydroxide, 20% solution.

Ascorbic acid, 5% solution freshly prepared.

Potassium cyanide, 5% solution freshly prepared.

Boric acid.

The solution of accurately weighed selenite, containing 0·4–4·0 mg of selenium, is neutralised in a 100-ml glass-stoppered Erlenmeyer flask in the presence of one drop of methyl red, diluted to 10 ml, and treated with 1 ml of ascorbic acid solution; the precipitated selenium is dissolved by the addition of 1 ml of a 5% solution of potassium cyanide and allowing the solution to stand for 10 minutes. When selenium has completely dissolved, 0·5 g of boric acid is added to the reaction mixture, its volume is increased to about 35 ml and the liquid is kept boiling for 10 minutes in order to remove excess cyanide. The evaporated water is periodically replaced. On cooling, the determination of the selenocyanide is completed as described elsewhere.[2]

The results obtained by the tungstate method are presented in Table I.

Some alterations to the earlier procedure are necessary for the distillation method, owing to the presence of dehydroascorbic acid. At higher temperature, under the conditions described, dehydroascorbic acid (more correctly, the product formed when ascorbic acid is oxidized by bromine) is capable of reducing selenium compounds of higher oxidation state (to elementary selenium when pH values are sufficiently low). During this process, compounds form which interfere with the iodometric measurements. This interference can, however, be eliminated when the oxidizing property of the medium is maintained throughout the distillation. An excess of a mixture of potassium bromate and potassium bromide may be used for this purpose.

THE DISTILLATION METHOD

Reagents

Most of these are as used in the tungstate method.[2] Sodium tungstate and bromine water are not required. Additional reagents are a solution containing 1% potassium bromate and 0·5 potassium bromide, 50% sulphuric acid and concentrated sulphuric acid.

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* According to the investigations of Brintzinger,[8] a dilute solution of selenite reacts with ascorbic acid at temperatures below 50°, with precipitation of colloidal selenium.

TABLE I. RESULTS BY THE TUNGSTATE METHOD

Na_2SeO_3 weighed *mg*	$0{\cdot}01N$ $Na_2S_2O_3$ consumed		Na_2SeO_3 found *mg*	Δ, %
	tests, *ml*	mean value *ml*		
8·243	9·49 9·48 9·46	9·48	8·198	−0·55
4·121	4·76 4·77 4·75	4·76	4·116	−0·12
1·652	1·91 1·91 1·90	1·91	1·652	0
0·818	0·96 0·95 0·95	0·95	0·822	+0·49

TABLE II. RESULTS BY THE DISTILLATION METHOD

Na_2SeO_3 weighed, *mg*	$0{\cdot}01N$ $Na_2S_2O_3$ consumed		Na_2SeO_3 found, *mg*	Δ, %
	tests, *ml*	mean value, *ml*		
8·243	9·54 9·58 9·57	9·56	8·264	+0·29
4·121	4·78 4·79 4·78	4·78	4·134	+0·32
1·652	1·93 1·92 1·92	1·92	1·660	+0·48
0·818	0·95 0·96 0·96	0·96	0·830	+1·46

Weighing, reduction, preparation of the cyanide solution and removal of excess cyanide are carried out as described earlier,[2] but these operations may be carried out in the 100-ml distillation flask. After removal of cyanide by boiling, the reaction mixture is treated with 10 ml of the bromate–bromide solution and 2 ml of sulphuric acid, the joints are greased with concentrated sulphuric acid, and the flask is connected to the condenser. The distillation is then concentrated as before.

Some results obtained by the distillation method are presented in Table II.

Zussammenfassung—Das Selenit kann bei entsprechendem pH-Wert der Lösung durch Askorbinsäure zu elementarem Selen reduziert werden. Letzeres in Selenocyanid übergeführt, welches endlich unter Verwendung von Wolframat, oder nach einer Destillation jodometrisch ermittelt werden kann.

Résumé—A un pH convenable, le sélénite peut être réduit par l'acide ascorbique. En le transformant en selénocyanure il peut être dosé avec précision par iodométrie à l'échelle micro. L'excès du réducteur est éliminé par le brome et l'influence gênante des bromures formés est éliminée comme précédemment.

REFERENCES

[1] E. Schulek and E. Körös, *Z. analyt. Chem.* 1953 **139,** 20.
[2] E. Schulek and L. Barcza, *Talanta* 1959, **3,** 23.
[3] H. Brintzinger, *Kolloid-Z.* 1937 **78,** 23.

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CONTRIBUTIONS TO THE CHEMISTRY OF SELENIUM AND SELENIUM COMPOUNDS—IV

DETECTION AND DETERMINATION OF MINUTE AMOUNTS OF SELENITE IN THE PRESENCE OF SELENATE

E. SCHULEK and L. BARCZA
Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary

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Summary—In the absence of halides, and at a low hydrogen ion concentration, selenite is reduced by ascorbic acid whereas selenate remains unchanged. By utilising this reaction, 0·01% of selenite can be detected in selenate preparations. The method also lends itself to quantitative determinations, since the reduced selenite may be converted into selenocyanide and determined by iodometry. It is possible to determine 1% of selenite in selenates by this method with a relative error of ±1%.

MÜLLER[1] has described the detection of selenite in the presence of selenate by reduction with sulphur dioxide, selenate remaining unchanged. The ratio of selenite to selenate is not mentioned, and only the limits of detection for the test (5 mg Se per litre) are given.

We find that the method is suitable for detecting selenite in the presence of a relatively small amount of selenate, but that when the quantity of selenite falls below 0·1 mg and that of selenate rises above 20 mg the method is unreliable.

Elsewhere[2] we have shown that the reduction of selenate to selenite (and through selenite to elementary selenium) is promoted by high hydrogen ion concentration, the presence of halide ion, and increased temperature; in moderate concentrations selenate is reduced to a negligible extent by ascorbic acid at room temperature in a nearly neutral solution free from halide, even over an extended period of time, but in identical conditions the precipitation of selenium from minute amounts of selenite (10 μg) can be observed visually in 5–10 minutes. On this basis a method is proposed for the detection of selenite in the presence of selenate.

Procedure. The test solution should contain not more than 0·1 g of Na_2SeO_4. Neutralise the solution, adjust the pH to a value of 6 using indicator paper, dilute to a volume of about 10 ml and treat with 1 ml of 5% ascorbic acid solution. Set aside for 10 minutes. Carry out a blank test in exactly the same way.

By this procedure the presence of 0·01% of selenite in selenate can be reliably indicated.

No methods described in the literature proved to be suitable for the determination of minute amounts of selenite in the presence of selenate. The thiosulphate method of Norris and Fay[3] can only be used on the macro scale, and the iodometric method of Klasson and Mellquist[4] does not yield accurate results, even when the experimental conditions are strictly maintained. Other methods based on the oxidation of selenite or on gravimetry cannot be considered as micro methods.

We have obtained excellent results by applying the tungstate-ascorbic acid reduction method to determination of selenite in the presence of selenate, and find that 0·1 g of selenate does not interfere, nor do sulphate, perchlorate or small amounts of chloride or bromide.

The sample may contain from 0·8 to 8·0 mg sodium selenite and from 0 to 100 mg of sodium selenate, and is treated precisely as described previously.[2] The results summarised in Table I show that 1 % of selenite can be determined in the presence of sodium selenate with a relative error of 1 %.

TABLE 1

Na$_2$SeO$_3$ *mg*	Na$_2$SeO$_4$, *mg*	Approx. mole ratio	0·01*N* Na$_2$S$_2$O$_3$ consumed		Na$_2$SeO$_3$ found, *mg*	Deviation %
			tests, *ml*	mean value, *ml*		
8·088	1	10 : 1	9·32 9·34 9·34	9·33	8·069	−0·21
4·044	5	1 : 1	4·67 4·66 4·66	4·66	4·030	−0·35
0·806	10	1 : 10	0·93 0·94 0·94	0·94	0·813	+0·88
	100	1 : 100	0·92 0·92 0·94	0·93	0·804	−0·25

The distillation method for the determination of selenite described at the same time as the tungstate method has also been examined and found to permit the determination of both selenite and selenate in the presence of each other. Details of this will be presented in a subsequent communication.

Zusammenfassung—In Abwesenheit von Halogeniden werden nur die Selenite bei Zimmertemperatur bei niedrigem pH-Wert der Lösung zu elementarem Selen reduziert; Selenate dagegen nicht. So kann noch 0,01 % Selenit neben Selenat nachgewiesen und jodometrisch über Selenocyanid bestimmt werden. Die Bestimmungsgrenze des Selenits in Selenat beträgt etwa 1 %.

Résumé—En l'absence d'halogénures et aux faibles concentrations d'ions hydrogène, le sélénite est réduit par l'acide ascorbique alors que le séléniate ne réagit pas. En utilisant cette réaction, on peut déceler 0,01 % de sélénite dans les préparations de séléniate. La méthode se prête aussi aux dosages quantitatifs par réduction du sélénite en sélénocyanure et par dosage iodométrique de celui-ci. Par cette méthode, on peut déterminer 1 % de sélénite dans le séléniate avec une erreur relative de ±1 %.

REFERENCES

[1] E. Müller, *Z. phys. Chem.*, 1922, **100**, 346.
[2] E. Schulek and L. Barcza, *Talanta*, 1959, **3**, 27.
[3] J. F. Norris and H. Fay, *Amer. Chem. J.*, 1896, **18**, 703.
[4] P. Klason and H. Mellquist, *Z. angew. Chem.*, 1912, **25**, 514.

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THE DETERMINATION OF ULTRA-MICRO QUANTITIES OF SILVER IN PLATINUM SPONGE BY NEUTRON-ACTIVATION ANALYSIS

D. F. C. MORRIS and R. A. KILLICK
Department of Chemistry, Brunel College of Technology, London, W.3

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Summary—The increasing availability of nuclear reactor facilities makes analysis by neutron-activation an important method for more widespread use in trace element analysis. The technique is advantageous for the determination of submicrogram quantities of silver in platinum sponge, and its application in this connection is described.

Activation of samples of platinum sponge has been carried out by neutron irradiation in the Harwell Pile BEPO for a period of one month, and silver has been assayed by measurements of the radionuclides ^{110m}Ag—^{110}Ag. Radiochemical separation after the addition of carrier has been based mainly on precipitations of silver as chloride, sulphide, oxide, and iodate, and on electrolytic deposition. The silver has been finally precipitated as the iodate and counted with a NaI crystal γ-scintillation counter. Chemical yields have been determined gravimetrically.

In order to avoid errors due to self-shielding, standards have been made by adding small known amounts of silver to analytical samples.

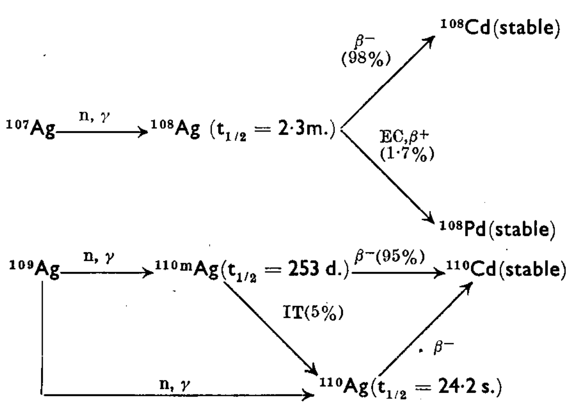
The precision of analyses has been better than ± 10 per cent, and the method described may be applied to the analysis of platinum containing as little as 0·02 ppm Ag. The ultimate sensitivity could be considerably enhanced by employing larger analytical samples and the Harwell Pile DIDO for irradiation.

INTRODUCTION

IN the production of precious metals it is necessary to have an accurate specification of trace impurities. Some of the impurities of consequence may be present in amounts below the sensitivity of conventional methods of analysis.

In the present work, neutron-activation[1–5] has been applied to the determination of silver in platinum sponge. The Harwell Pile BEPO has been used as the neutron source. It has been estimated[5] that under ideal circumstances the use of this reactor will enable the determination of as little as *c.* 5×10^{-9} g of silver with a precision of $\pm 10\%$.

Silver has two stable isotopes ^{107}Ag (% abundance 51·35) and ^{109}Ag (% abundance 48·65), which on irradiation with thermal neutrons undergo the nuclear reactions—



The thermal neutron-activation cross sections for the stable silver isotopes are[6]:

$$
\begin{array}{ll}
{}^{107}\mathrm{Ag}(n,\gamma){}^{108}\mathrm{Ag} & \sigma = 44 \text{ barns} \\
{}^{109}\mathrm{Ag}(n,\gamma){}^{110m}\mathrm{Ag} & \sigma = 2{\cdot}8 \quad ,, \\
{}^{109}\mathrm{Ag}(n,\gamma){}^{110}\mathrm{Ag} & \sigma = 110, \quad ,,
\end{array}
$$

and a summary of nuclear data for the different radioisotopes of silver produced in the nuclear reactions[7] is given in Table I.

TABLE I. SUMMARY OF NUCLEAR DATA FOR RADIOISOTOPES OF SILVER

Radioisotope	Half-life	Radiations and energies, *MeV*
^{108}Ag	2·3 min.	β^- 1·77; (EC; γ 0·43, 0·60; β^+)
^{110m}Ag–^{110}Ag	253 days	β^- 0·530 (35%), 0·087 (58%), 2·12 (3%), 2·82 (3%); γ 0·116 to 1·51
^{110}Ag	24·2 sec	β^- 2·16 (60%), 2·84 (40%); γ 0·66, 0·94 (weak), others.

For the present purpose, a procedure involving chemical separation and radiometric assay of the radionuclides ^{110m}Ag—^{110}Ag from neutron irradiated samples of platinum has been developed.

EXPERIMENTAL

Samples for analysis

The material analyzed consisted of platinum sponge supplied by the Mond Nickel Co. This was given no chemical treatment before irradiation. Samples consisting of *c.* 0·3 g of small fragments were weighed out accurately into irradiation containers made from 4-mm internal diameter silica tubing, which were then sealed. Just as in any other sensitive analytical method, extensive precautions must be taken to avoid contamination at this stage.

Neutron irradiation of samples and standards

In order to avoid self-shielding differences with samples and standards,[5] standards were prepared by adding known small quantities of silver to platinum samples to be analyzed. This was done by adding aliquot portions of a dilute standard solution of silver, and a drop of wetting-agent, to 0·3 g samples of the platinum sponge in silica irradiation tubes. The liquid in the tubes was allowed to soak into the metal sponge, and then was carefully evaporated to dryness, after which the tubes were sealed.

Standards containing the added silver and samples to which no silver had been added, were packed with glass wool into a standard 3 in. × 1 in. aluminium can for irradiation in BEPO. Irradiation was for one month. On delivery from Harwell after irradiation, the samples and standards were analyzed radiochemically for ^{110m}Ag—^{110}Ag by the procedure described below.

Chemical separation

A radiochemical separation procedure using carrier chemistry was used to secure the necessary separation of silver. In order to attain solution of the samples and satisfactory separation of silver, a procedure had to be developed which was rather different from that employed by Morris and Killick[8] for the radioactivation analysis of silver in galena and blende.

In the present work, irradiated samples and standards have been dissolved in *aqua regia.* Silver has been initially separated as the ammine complex followed by precipitation of the chloride from nitric acid solution. The silver has been purified further by ferric hydroxide scavenging and silver sulphide precipitation, both carried out in ammoniacal solution. After a further precipitation of the chloride, the silver has been purified by electrolysis,[9] and has finally been converted to the iodate $AgIO_3$, in which form it has been counted.

The efficiency of silver chloride precipitation and of electrodeposition as decontamination steps for silver has been indicated by the tracer tests of Sunderman and Meinke.[9]

Reagents

Ag carrier: 10 mg Ag/ml (added as $AgNO_3$ in very dilute HNO_3) standardised.
Fe^{III} carrier: 10 mg Fe/ml (added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl).
Aqua regia: 4 parts conc. HCl + 1 part conc. HNO_3 (v./v.).
HCl; *M*.
HCl; 6*M*.
HNO_3; 6*M*.
HNO_3; conc.
Cyanide plating solution: mix 7 ml of 3*M* NaCN with 1 ml 5*M* NaOH.
H_2SO_4; conc.
KIO_3; saturated solution.
NaOH; 6*M*.
NH_4OH; 6*M*.
$(NH_4)_2S$; saturated solution.
Manoxol OT; (British Drug Houses Ltd.), 0·1% solution in water.
Ethyl alcohol; 95%.

Preparation and standardisation of silver carrier

Dissolve 15·75 g of $AgNO_3$ in a minimum amount of H_2O, add a few drops of HNO_3, and dilute the solution to 1 litre.

Pipette exactly 5 ml of the carrier solution into a 50-ml centrifuge tube and dilute to 20 ml with H_2O. Add 1 ml of saturated KIO_3 solution and stir to coagulate the precipitate which forms. Add an additional drop of KIO_3 to test for completeness of precipitation. Filter the precipitate into a weighed sintered-glass crucible of grade 3 or 4. Wash the precipitate with 5 ml of 95% ethyl alcohol and dry in an oven at 110° for 15 min. Cool and weigh as $AgIO_3$.

Radiochemical separation procedure

Step 1: Remove the silica tubes from the can, open them at the constriction, and transfer the solid samples to 50-ml beakers. Wash out the tubes with a little warm dil. HNO_3 and transfer the washings quantitatively to the beakers.

Step 2: To a sample in a 50-ml beaker with a watch glass as cover add 2 ml of standard Ag carrier and 5 ml of *aqua regia*. Dissolve the platinum by heating on a water bath. Evaporate carefully to small volume under an infrared lamp, and then add 10 ml of distilled H_2O. Stir for 5 min. Add 2 ml of conc. NH_4OH dropwise with vigorous stirring. Digest at 60° for 10 min and allow the orange–yellow precipitate of ammonium chloroplatinate to settle. Decant off the supernate into a clean 50-ml centrifuge tube, add a further 1 ml of conc. NH_4OH to the residue in the beaker, digest, and decant the supernate into the centrifuge tube. Filter the solution into a clean 50-ml centrifuge tube. (Note *a*).

Step 3: Add a few drops of Manoxol OT solution and heat to boiling (Note *b*). Add 6*M* HNO_3 drop by drop until precipitation of AgCl is complete. Heat until the AgCl has coagulated. Centrifuge and discard the supernate.

Step 4: Wash the precipitate three times with 10-ml portions of hot H_2O. Dissolve the AgCl in 2 ml of conc. NH_4OH (Note *c*). Dilute to 20 ml with H_2O and add 1 ml of Fe^{III} carrier. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube, and discard the precipitate.

Step 5: To the solution add 1 ml of saturated $(NH_4)_2S$ solution. Stir vigorously and centrifuge. Discard the supernate.

Step 6: Dissolve the Ag_2S precipitate by heating with 1 ml of conc. HNO_3. Dilute to 20 ml with H_2O, centrifuge, and discard any S residue.

Step 7: To the solution add a few drops of Manoxol OT solution and heat to boiling. Add 6*M* HCl drop by drop until precipitation of AgCl is complete. Heat until the AgCl has coagulated. Centrifuge and discard the supernate.

Step 8: Dissolve the AgCl in 8 ml of cyanide plating solution (Note *d*). Mix the solution thoroughly transfer to a Pregl micro-electrolysis apparatus and electrolyse at 4 volts for 15 min. When electrolysis is complete, remove the electrodes and wash the cathode with H_2O from a wash bottle for 1 min.

Step 9: Dissolve the Ag completely off the cathode with conc. HNO_3 and transfer the solution to a clean 50-ml centrifuge tube. Add 10 ml of H_2O. Repeat Steps 7 and 8.

Step 10: Dissolve the Ag completely off the cathode with conc. HNO_3 and transfer the solution to a clean 50-ml centrifuge tube. Make the solution alkaline with 6*M* NaOH, and add 3 drops in excess. Centrifuge the Ag_2O precipitate and discard the supernate. Dissolve the Ag_2O in 4 drops of conc. H_2SO_4 and evaporate completely to dryness (Note *e*). Cool.

Step 11: Add 20 ml of H_2O and boil until a clear solution is obtained, then add 1 ml of saturated KIO_3 solution. Centrifuge and discard the supernate.

Step 12: Dissolve the $AgIO_3$ precipitate in 4 drops of conc. NH_4OH. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube.

Step 13: Add 3 drops of conc. H_2SO_4 to the solution. Centrifuge the $AgIO_3$ precipitate and wash twice with H_2O and once with 5 ml of 95% ethyl alcohol.

Step 14: Slurry the precipitate with 95% ethyl alcohol on to a weighed aluminium counting tray (A.E.R.E. cat. No. 4-3/1068), by using a transfer pipette. Make sure that the distribution of the precipitate on the tray is uniform. Dry at 110° for 15 min and weigh to establish the chemical yield (20 mg Ag $\equiv$ 52·43 mg $AgIO_3$).

Notes

(*a*) The procedure must be followed carefully to ensure complete exchange of radiosilver and carrier.

(*b*) The addition of Manoxol OT helps to coagulate the AgCl and to prevent its adherence to the walls of the tube.

(*c*) A little heating may be necessary.

(*d*) See reagents.

(*e*) It is not necessary to remove the last traces of H_2SO_4 on the walls of the tube.

Counting of the isolated silver iodate precipitates

In the present work the final precipitates of $AgIO_3$ were counted with a NaI(Tl) γ-scintillation counter type 1186 A, fitted with conventional associated electronic equipment. Each sample was placed on shelf 2 of the lead castle, a standard Al—Pb sandwich absorber being inserted on shelf 1 between the sample and the detector. A statistical accuracy of 0·5% was achieved by measuring a total of 40,000 counts, where practicable. In cases where the activity was low, counting was carried out for a period of 40 min. All measured activities were corrected for background and chemical yield. No paralysis correction was necessary.

The counting rates of samples were measured over a period of two weeks, and the decay corresponded to the measurement of ^{110m}Ag—^{110}Ag activity, no short-lived contaminants being detected unless the discriminator bias was set low.

As a check, the γ- spectra of precipitates were recorded using an IDL γ-scintillation spectrometer of the recording type, and no photoelectric peaks other than those due to ^{110m}Ag—^{110}Ag were detectable (Fig. 1). Spectra were also measured on a manually operated IDL γ-spectrometer fitted with a scaling unit, enabling better sensitivity and counting statistics. In this case also, only peaks due to ^{110m}Ag—^{110}Ag could be detected.

Assay of the precipitates by Geiger–Müller counting was not desirable, since with this type of detector decay measurements showed the presence of a very small trace of contaminant, believed to be radioplatinum.

RESULTS

If A_1 is the silver activity (corrected for background and chemical yield) for a standard containing w μg of added Ag, and A_2 is the corrected activity of a corresponding sample of the same weight but with no added Ag, it follows that an activity of A_1–A_2 corresponds to w μg of Ag. The silver content of samples may therefore be calculated from their corrected counting rates.

Typical analysis results obtained by the neutron-activation method are shown in Table II.

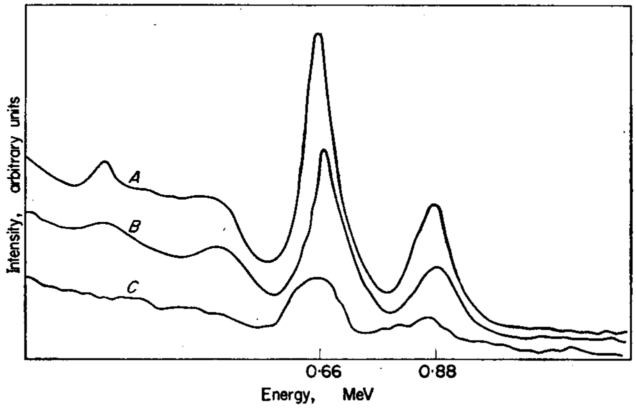


FIG. 1. Gamma spectra. A, pure ^{110m}Ag—^{110}Ag sample. B, final precipitate from a platinum analysis standard. C, final precipitate from a platinum analysis sample.

DISCUSSION

Attention must be given to possible errors caused by the presence of elements other than silver in samples, which may give rise to the radionuclides ^{110m}Ag—^{110}Ag on neutron irradiation. The elements cadmium and indium demand consideration. These elements could possibly give rise to ^{110m}Ag—^{110}Ag activity by the following nuclear reactions—

$$^{110}Cd(n,p)^{110m}Ag$$

$$^{113}In(n,\alpha)^{110m}Ag$$

These nuclear changes are liable to occur with fast neutrons, which may be present to an extent of *c.* 10% of the slow neutron flux in the case of irradiations used in the present work. An estimate of possible interference has been made by irradiating small samples of pure CdO and In_2O_3, together with pure Ag standards in the Pile. The silver activity of the samples was chemically separated, and counted as before. The results indicated that if a sample of platinum sponge contained 1 ppm of cadmium and 1 ppm of indium, the maximum spurious silver content would be only *c.* 0·00004 ppm.

Any interference of consequence due to the production of silver radionuclides other

TABLE II.—SILVER CONTENT OF SAMPLES OF PLATINUM SPONGE DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample C Pt 58	Sample C Pt 46
0·48 ppm	0·24 ppm
0·43	0·24
0·44	0·27
0·45	0·28
0·41	0·29
0·40	0·26
Av. 0.44	Av. 0·26

than ^{110m}Ag—^{110}Ag should have been apparent from energy and decay measurements made on the counted final precipitates from platinum samples.

The neutron-activation method described in this paper may be applied to the analysis of samples of platinum containing as little as 0·02 ppm Ag.* The ultimate sensitivity of the method could be considerably enhanced by employing larger samples or the Harwell Pile DIDO as neutron source.

Precision (standard deviation) of radio-activation analyses has always been better than ±10%.

Since platinum apparently can only be dissolved in *aqua regia*, other methods of analysis requiring the bringing of samples into solution would be likely to be bedevilled by problems of silver adsorption, even if the method potentially provided satisfactory analytical sensitivity. Errors due to contamination of reagents would also have to be taken into account.

In addition, conventional emission spectrographic methods do not provide sufficient sensitivity for the reliable determination of silver in platinum.

Neutron-activation analysis clearly has a number of unique advantages for the determination of silver and other trace elements in platinum, and only quite small samples of the precious metal are required for accurate analysis.

Acknowledgement—The authors wish to express their gratitude to the Mond Nickel Co. for financial assistance to one of them (R. A. K.)

Zusammenfassung—Je mehr Reaktoren zur Verfügung stehen, desto höhere Bedeutung kommt der Neutronenaktivierungsanalyse für breite Anwendung bei Spurenanalyse zu. Die Methode ist von Vorteil bei der Bestimmung von Submikrogrammengen von Silber in Platinschwamm. Die Anwendung der Methode auf dieses Problem wird beschrieben.

Die Aktivierung von Platinschwammproben erfolgte durch Neutronenbestrahlung im Harwell-Reaktor BEPO über einen Zeitraum von einem Monat. Die Messung basierte auf dem Vorgang ^{110m}Ag–^{110}Ag. Radiochemische Trennung nach Zugabe eines Trägers erfolgte durch Abscheidung des Silbers als Chlorid, Sulfid, Oxyd und Iodat, sowie elektrolytisch. Das Silber wurde zuletzt als Jodat gefällt und die Zählung mit einem NaI Gamma-Scintillations-Zähler durchgeführt. Chemische Analysen wurden gravimetrisch durchgeführt.

Um Fehler durch Selbstabschirmung zu vermeiden, wurden Standardproben durch Zugabe kleiner, bekannter Silbermengen zu analytischen Proben hergestellt. Reproduzierbarkeit der Methode ist besser als ±10%. Die Methode kann für die Bestimmung von bis herab zu 0,02 ppm Ag verwendet werden. Die analytische Empfindlichkeit konnte erheblich gesteigert werden durch Verwendung grösserer Proben und Bestrahlung im Harwell-Reaktor DIDO.

Résumé—Les possibilités d'utilisation croissantes du réacteur nucléaire font de l'analyse par activation par neutrons une méthode importante dont l'emploi doit être plus répandu dans l'analyse de traces d'éléments. La technique est avantageuse pour le dosage de submicrogrammes d'argent dans la mousse de platine, et l'auteur décrit l'application à ce cas.

L'activation d'échantillons de mousse de platine a été réalisée par l'irradiation par neutrons dans la pile BEPO de Harwell et l'argent a été dosé par la détermination des radio éléments ^{110m}Ag—^{110}Ag.

La séparation radiochimique après addition d'un entraineur a été basée principalement sur des précipitations de l'argent à l'état de chlorure, sulfure, oxyde et iodate et sur le dépôt électrolytique. L'argent a finalement été précipité à l'état d'iodate et dosé avec un compteur gamma à scintillation à cristal de NaI. On a determiné les rendements chimiques par gravimétrie.

Afin d'éviter des erreurs dues à l'absorption propre on a fait des étalons en ajoutant de faibles quantités connues d'argent à des échantillons analytiques.

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* The sensitivity limit has been set at a content sufficient to give 40 counts/min above the γ-counter background.

La précision des analyses est meilleure que ±10%, et on peut appliquer la méthode décrite à l'analyse de platine contenant des quantités aussi faibles que 0,02 p.p.m. d'argent. On pourrait améliorer considérablement cette dernière sensibilité en employant des échantillons analytique splus importants et la pile DIDO de Harwell pour l'irradiation.

REFERENCES

[1] G. E. Boyd, *Analyt. Chem.*, 1949, **21**, 335.
[2] A. A. Smales, *Atomics*, 1953, **4**, 55.
[3] W. W. Meinke, *Science*, 1955, **121**, 177.
[4] R. C. Plumb and J. E. Lewis, *Nucleonics*, 1955, **13**, No. 8, 42.
[5] E. N., Jenkins and A. A. Smales, *Quart. Revs.*, 1956, **10**, 83.
[6] AEC Neutron Cross Section Advisory Group, U.S.A.E.C. document, AECU 2040 and supplements.
[7] S. Strominger, J. M. Hollander, and G. T. Seaborg, *Revs. Mod. Phys.*, 1958, **30**, 585.
[8] D. F. C. Morris and R. A. Killick, *Analyt. Chim. Acta*, 1959, **20**, 587.
[9] D. N. Sunderman, and W. W. Meinke, *Analyt. Chem.*, 1957, **29**, 1578.

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THE WET OXIDATION OF BONE.

DIGESTION WITH 100 PER CENT SULPHURIC ACID FOLLOWED BY THE ADDITION OF DIOXONIUM PERCHLORATE

G. FREDERICK SMITH and HARVEY DIEHL
Noyes Chemical Laboratories, University of Illinois, Urbana, and
Iowa State College, Ames, Iowa, U.S.A.

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Summary—Organic materials rich in fat, such as bone and bone marrow, introduce complications in wet ashing by previously described procedures. In the accompanying detailed procedure, 100% sulphuric acid and 73.60% perchloric acid serve as oxidants with vanadium as catalyst. Reagent preparation, apparatus design, and illustrative reactions are described.

INTRODUCTION

THE wet oxidation of bone, in preparation for the trace element determination of metallic components, presents unusual operational prerequisites. The presence of fat as a principal component in both the solid composition and the bone marrow complicates destructive oxidation. The trace element estimation of lead or beryllium are illustrative. Medical autopsy and forensic investigations of industrial hazards are frequently involved.

The regular procedures of wet ashing require modification. For bone tissue and bone marrow a two-stage oxidation reaction is requisite.

A preliminary oxidation employing 100% sulphuric acid as oxidant is applied. The thoroughly carbonized sample thus treated is subjected to a second stage reaction. The completion of destructive oxidation is provided by the addition of 73.6% perchloric acid. The first stage involves boiling temperatures of 300° to 325°. The resulting reaction mixture is thus effectively carbonized. The second stage of completed oxidation is operative at 200° to 210°. A milligram of vanadium is added as catalyst. Total reaction time is 30 minutes or less for controlled oxidation. The process is at no disadvantage because of associated hazard.

PREVIOUS STUDIES IN WET OXIDATION

Mixed nitric and perchloric acids in wet oxidation procedures for a wide variety of natural and synthetic organic compositions, has been described.[1] From this work and publications therein cited, routine analytical procedures for a great number of trace metals and major constituents have been applied.

For the wet oxidation of organic materials predominantly composed of cellulose proteins, or sugars, selected and maintained concentrations of perchloric acid alone are admirably adequate.[2] By this procedure selected graded oxidation potentials may be rigidly controlled. The trace element determination of copper in food packaging paper is illustrative.

Organic compositions such as alkaloids and other heterocyclic ring nitrogen compounds, gas-mask canister carbon, decolorizing carbon, or ion-exchange resins require high oxidation potentials for their rapid oxidation. Digestion with mixed sulphuric and perchloric acids serves best.[3] The very highest oxidation potentials, graded in magnitude, and continuously controlled, are thus made operative.

In broad scope, the problem in wet oxidation procedures demands oxidation potentials of 0.8 to 2.0 volts or more. Reaction potentials must be rigidly controlled at selected intermediate values depending upon the type of organic matter to be oxidized.

Chromium, vanadium and molybdenum have been selectively applied as reaction catalysts.

Nitric, sulphuric and perchloric acids are the most important oxidants. Their individual, simultaneous, and stepwise application accounts for a wide diversity of experimental conditions. Selective use, order of addition, and the temperatures involved are important operational variables.

The procedures are free of hazard, rapid in prosecution, and precise in estimation of either trace metals or macro magnitude, non-volatile components. Because of their use, dry ashing procedures are largely losing favour.

THE PRESENT STUDY

The present research involves the wet ashing of bone tissue, bone marrow, and bone-adherent muscle tissue. The problem is complicated by the presence of fat as a major constituent. Such material in the process of wet oxidation, following previously described procedures, requires the oxidation of samples of limited size if uncontrolled reaction intensity is to be avoided. Therefore recourse is had to a procedure involving a two-stage oxidation.

The first reaction involves the decomposition of organic matter to form carbon, or degradation carbonaceous products suspended in or soluble in mineral acid. This is accomplished by high temperature digestion with concentrated sulphuric acid. The second stage involves the addition of concentrated perchloric acid at materially lowered temperature. The oxidation of carbon and acid-soluble degradation products of the preliminary digestion is thus rapidly completed. A few milligrams of vanadium serves to catalyze the second-stage reaction.

EXPERIMENTAL

Reagents employed

100% *sulphuric acid*: Made by mixing 96–97% (reagent grade) sulphuric acid with the necessary amount of 15–18% fuming sulphuric acid. A weight of 337.5 g of reagent grade acid is added to 453 g of the oleum. By analysis the resulting acid was found to be 99.5% H_2SO_4. M.p. 10.5°c. Sp.Gr. (25°/4°) = 1.837. For preparation of 100% acid, employing oleum of different SO_3 content, the following formula, as devised by Gerster,[4] is applicable:

$$X = 100\,(b - a)/(a - c)$$

where X = quantity of sulphuric acid to be added to 100 parts of oleum,
a = total SO_3 per 100 parts of the acid desired,
b = total SO_3 per 100 parts of the original oleum,
c = total SO_3 per 100 parts of the acid used for dilution.

If the SO_3 content of the oleum is not known a close approximation to the desired 100% sulphuric acid can be made by determining the boiling point of a given reagent grade acid after the addition of increasing amounts of oleum. Sulphuric acid of 100% H_2SO_4 content has a boiling point of 325° at approximately 750 mm atmospheric pressure. By examination of the results in Fig. 1 this procedure is seen to be less accurate because of the limited increase in boiling point with increase in concentration of SO_3.

Dioxonium perchlorate (*73.6% perchloric acid*): Made by vacuum distillation of 72.5% acid (the perchloric acid-water azeotrope) at 2–7 mm pressure as described by Smith and Koch.[5]

Vanadium catalyst: Ammonium vanadate or vanadic oxide.

Apparatus assembly

The apparatus, as originated by Bethge,[2] and employed in previous procedures in wet oxidations, was again employed. To provide for the disposal of evolved SO_2 from the oxidation of organic matter by sulphuric acid, the top terminal of the water cooled condenser is fitted with an adaptor. A small-bore rubber tube conducts away the SO_2 which is vented into the sink drain for absorption in running water. The Bethge apparatus, manipulations, and manner of use, have been previously described.[2]

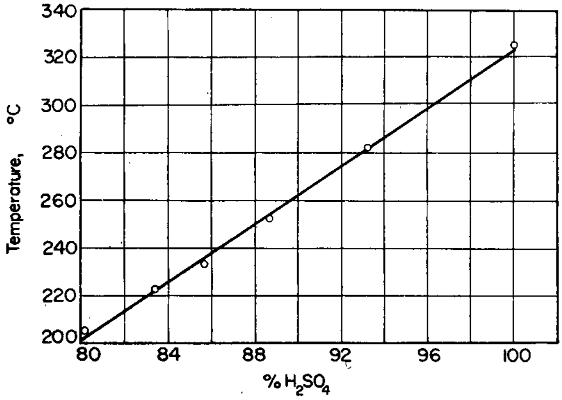

FIG. 1.

Test sample selection

Small diameter fore-leg bone of young beef carcase was cut into 5 mm thick discs. No attempt was made to remove adhering cartilege. The bone centre was left intact. These bones slices were then diced into fragments of 10-mm maximum dimension.

Bone samples from beef of varying ages were not tested. The presence of soft marrow in bone from very young animals would react towards boiling 100% sulphuric acid with similar formation of precipitated carbon and soluble carbon degradation products. The second stage of oxidation, following the addition of perchloric acid, would not be altered materially in carbonaceous residue.

Digestion of sample

Three samples, 0.5, 1.6, and 3 grams, were consecutively wet ashed. The larger the sample taken the lower the boiling temperature becomes for a given volume of sulphuric acid in the first stage of oxidation. This is due to dilution by the resulting reaction products. For the larger sample weights the volume of sulphuric acid should be increased. Otherwise the boiling temperature falls materially below 325°.

The sulphuric acid digestion is complete when SO_2 is no longer evolved. Further digestion for the first stage reaction is then of little value. The heating is then discontinued and the reaction temperature allowed to fall to approximately 200°. The second stage of oxidation, following the addition of 73.6% perchloric acid, is rapid and exothermic.

The results of the digestions are given in Tables I, II, and III.

REACTION CHARACTERISTICS

100 per cent sulphuric acid is employed in the first stage destructive carbonization reaction to shorten the required reaction time. The boiling temperature should be in the range 315° to 325°. Increase in sample weight requires increase in sulphuric acid.

Reaction degradation products lower the boiling temperature. This is illustrated by the results in Tables I, II, and III.

The use of 100% H_2SO_4 prevents formation of insolubles in the wet ash residue. The use of lesser concentrations accompany their precipitation.

Boiling 100% H_2SO_4 requires 300 minutes for the complete wet ashing of 0.5 g of chrome tanned leather, and 240 minutes for 1 g of cellulose at 325°.

TABLE I. WET OXIDATION OF 0.5-G SAMPLE OF BONE

10 ml of 100% H_2SO_4 plus 1.0–2.0 mg of vanadium in first-stage reaction.
5 ml of 73.6% $HClO_4$ for the second stage of digestion.
Bethge apparatus with 250-ml reaction flask and SO_2 disposal vent.

100% H_2SO_4 digestion			73.6% $HClO_4$ digestion		
Reaction time, *min*	Temp, *degrees C*	Reaction effects	Reaction time, *min*	Temp, *degrees C*	Remarks
Start	28		21	195	$HClO_4$ 73.6% added
3	210	Reactants darken	22	160	Reaction exothermic
4	240	Minimum side wall deposit	23	201	Reaction complete
5	306	Solution dark chocolate colour	24	210	Solution clear
6	313	Solution in ebullition			
7	318	Exothermic reaction			
8	323				
10	317	Exothermic reaction completed			
12	318				
15	319	Discontinue heating			

In the preliminary oxidation period some volatile reaction product, which escapes through the SO_2 reaction drain tube, is evolved in the wet ashing of bone. The product condenses to a fluffy white, water-insoluble material of undetermined structure.

By elevating the temperature slowly during sulphuric acid digestion, cleaner reaction-flask walls result. This advantage is minor. Boiling 100% sulphuric acid refluxes these black deposited products down the flasks walls rapidly. This stage of reaction demands no attention.

If desired, the addition of 73.6% perchloric acid may be made in 1-ml portions. By this modification less acid is often required. Little additional reaction time is thus consumed.

OTHER APPLICABLE REACTIONS

Biological tissues such as heart, lung, liver, hair collagen or fat-free protein structures (or blood fibrin) may be wet ashed without complications following procedures previously described.[1,2] Fat-laden materials require the procedure as described because their perchloric acid degradation products, or their original structure, makes them acid-immiscible. Neither, in this case, is the presence of nitric

TABLE II. WET OXIDATION OF 1.6-G SAMPLE OF BONE

10 ml of 100% H_2SO_4 plus 1–2 mg of vanadium in first-stage reaction.
5 ml of 73.6% $HClO_4$ for the second stage of digestion.
Bethge apparatus with 250-ml reaction flask and SO_2 disposal vent.

100% H_2SO_4 digestion			73.6% $HClO_4$ digestion		
Reaction time, *min*	Temp, *degrees C*	Reaction effects	Reaction time, *min*	Temp, *degrees C*	Remarks
Start	26		18	210	73.6% $HClO_4$ added
4	250	Reactants black	19	178	Heat continued
5	266	Reaction refluxing	20	205	Solution red-brown
6	272	Inside flask walls clearing	21	209	Reaction exothermic
8	288	Exothermic effect shown	22	211	Turbid solution White deposit
10	283	Exothermic reaction over	23	214	Reaction complete
12	284				
14	285	SO_2 evolution over			
15	286	Discontinue heating			

TABLE III. WET OXIDATION OF 3.0-G SAMPLE OF BONE

15 ml of 100% H_2SO_4 plus 1–2 mg of vanadium in first-stage reaction.
5 ml of 73.6% $HClO_4$ for the second stage of digestion.
Bethge apparatus with 250-ml reaction flask and SO_2 disposal vent.

100% H_2SO_4 digestion			73.6% $HClO_4$ digestion		
Reaction time, *min*	Temp, *degrees C*	Reaction effects	Reaction time, *min*	Temp, *degrees C*	Remarks
Start	27		18	222	
1	50	Solution dark brown	19	196	73.6% $HClO_4$ added
2	165	Slight foaming	19.5	180	Heat continued
3	215	Solution black	20	205	Solution red-brown
5	268	Solution refluxing	21	213	Reaction exothermic
8	295	Inside flask walls clear	22.5	215	No turbidity formed
10	312		23	215	Reaction complete
12	322				
15	323	Discontinued heating			

acid a solution to the problem. Such two-phase systems, with fats supernatant in contact with boiling perchloric acid and its fumes, do not oxidize smoothly. Fires are ordinarily produced. Fumes of boiling perchloric acid in the presence of volatilized fat may lead to uncontrolled reaction kinetics. The use of boiling 100% sulphuric acid in a single stage reaction obviates this complication.

It is reasonable to apply the method as described to the wet ashing of cream, butter, cheese, lecithin or egg yolk.

Zusammenfassung—Stark fetthaltiges, organisches Material, wie Knochen und Knochenmark, verursacht Schwierigkeiten bei der nassen veraschung nach bekannten Methoden. In der hier vorgeschlagenen Methode werden 100%ige Schwefelsäure und 73.6%ige Perchlorsäure unter Zugabe von Vanadin als Katalysator verwendet. Bereitung der Reagenzien, verwendete Apparatur sowie Reaktionsbeispiele werden mitgeteilt.

Résumé—Des matériaux organiques riches en graisse comme l'os et la moelle, introduisent des complications dans la minéralisation par voie humide dans le cas des méthodes décrites précédemment. Dans le mode opératoire détaillé décrit ici, on utilise comme oxydants de l'acide sulfurique à 100% et de l'acide perchlorique à 73,60% avec le vanadium comme catalyseur. On décrit la préparation du réactif, l'étude de l'appareil et des exemples de réactions.

REFERENCES

[1] G. Frederick Smith, *Analyt. Chim. Acta*, 1953, **8**, 397.
[2] *Idem, ibid.*, 1957, **17**, 175.
[3] Harvey Diehl and G. Frederick Smith, Talanta, 1959, **2**, 209.
[4] M. Gerster, *Chem.-Zeit*, 1887, **11**, 3.
[5] G. Frederick Smith and E. G. Koch, *Ind. Eng. Chem. Anal.* 1931, **3**, 52.

Talanta, 1959, Vol. 3, pp. 47 to 53. Pergamon Press Ltd. Printed in Northern Ireland

THE APPLICATION OF ZONE ELECTROPHORESIS AND POLAROGRAPHY TO THE ANALYSIS OF COMPLEXONE MIXTURES

W. HOYLE and T. S. WEST
Chemistry Department, The University, Edgbaston, Birmingham 15, England

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Summary—A method of differentiating various types of polyaminocarboxylic acids (complexones) by paper electrophoresis of their cupric chelates at pH 5 is described; some migration rates are noted. The separated chelates may be removed from the pherogram and examined by polarography in 0·4*M* acetic acid. In many cases the $E_{\frac{1}{2}}$ values and the electrophoretic migration rate (M_I) serve to characterise the complexone. By the use of a standard curve relating observed $\triangle E_{\frac{1}{2}}$ values to known log *K* values, an estimate of the stability of the copper chelate may be obtained.

INTRODUCTION

IN the course of work on the synthesis of new complexones[1,2] it was found necessary to evolve some method of evaluating the final products and intermediate derivatives. The two common methods of preparation of complexones, the chloroacetic acid condensation with the amine, and the hydrolysis of the corresponding nitrile, both yield partially substituted products. Previously, unless the product was isolated, information about the complexone could not be obtained. The proposed method of investigation now enables the copper chelates of the complexones to be isolated by zone electrophoresis on paper and their approximate stabilities to be determined polarographically; this proves especially useful with acid soluble complexones. The method may also be used to follow the reaction of sterically crowded amines, e.g. *cyclo*hexane-*cis*-1:2-diamine,[2] with chloroacetic acid, and the hydrolysis of recalcitrant nitrile intermediates, for example, 4-methylcyclohexane-1:2-diamine-N:N:N′:N′-tetra-acetonitrile.[1,2] The electrophoresis technique enables synthetic mixtures containing, for example, IDA, NTA, and EDTA to be separated and characterised.

ELECTROPHORESIS

EDTA has been used in the electrophoretic separation of cations,[3] but the separation of complexones has not been reported. In early experiments we separated several complexones by electrophoresis at pH 5 and pH 10, but found difficulty in detecting their position, either by ninhydrin or by some weak, coloured calcium complex, such as calcium-phthalein complexone. Subsequently we followed the migration of the copper^{II} chelates which have the advantage of being blue in colour. An increase in sensitivity was obtained by spraying the paper with acidified potassium ferrocyanide solution, or with a solution of dithio-oxamide. The more stable copper chelates are only slowly developed by this latter reagent. The migration of ferric chelates was also examined,[4] but apart from the possibility of improved separation of mono- and di-carboxylic acids, they offered no advantages in our experiments.

The effect of compounds such as glycollic acid, ethylenediamine and cyanide ion, which might be expected to be present with complexones in reaction mixtures was examined. No interference was observed from glycollic acid or ethylenediamine, both of which yielded almost stationary spots. On the other hand, cyanide ion caused streaking due to the formation of a variably charged anionic complex with copper.

When a suitable technique had been evolved the migration rates of the chelates were determined relative to Cu^{II}-IDA, which was adopted as standard with an arbitrary migration rate of 1 relative to the origin. End-osmotic and capillary flow, and hence the true position of the origin, was determined by the use of glucose. The migration rates of a number of copper chelates were determined in order to establish empirically the relationship between migration rate and the number of carboxylic acid groups in the complexone molecule. This enabled a preliminary classification of known complexones to be made. The resolution of mono- and di- acids in admixture is often incomplete. This problem was not pursued further since complexones are classified as derivatives of imino$\underline{\text{diacetic}}$ acid.

These migration rates are listed in Table 1; where

$$M_I = \frac{\text{Distance moved by chelate relative to glucose}}{\text{Distance moved by IDA chelate relative to glucose.}}.$$

The distances were measured from the leading edges of the spots, i.e. the anode edge of the chelate spots and the cathode edge of the glucose spots. Complexones which contain more than two co-ordinating centres, *e.g.* diethylenetriaminepentaacetic acid, (DTPA), have a tendency to give more than one spot; these complexones clearly yield two migrating species (M_{I_1}, M_{I_2}) in the presence of excess copper solution, and generally the resulting spots are less well defined due to streaking. These results are also listed in Table I.

As a result of this investigation the complexones have been divided into three groups depending on their migration rates. With the exception of Chel ME, Chel DE, and DTPA, all of which gives two spots, the number of carboxylic acid groups in the molecule is equal to the group number plus one. It must be emphasised that the variation in M_I values within the group is not very significant due to a potential experimental error of $\pm 10\%$. The appearance of two migratory species from a single complexone in the presence of excess copper solution is indicative of more than two co-ordination centres in the molecule.

POLAROGRAPHIC EXAMINATION OF CHELATES ISOLATED BY ELECTROPHORESIS

We have previously shown that the polarographic half-wave potentials of the copper chelates of complexones in solution are directly related to the stability of these chelates.[5] In the present study we have therefore extended this relationship to the copper chelates separated by paper electrophoresis. In this manner data were obtained on very small amounts of material.

The elution of the copper chelates from the paper with water proved simple, and duplicate determinations showed uniform extraction. Under the experimental conditions used, the half-wave potential of a copper chelate depends on its concentration.[5] In dealing with solutions containing 50% excess of EDTA the half-wave potential of the EDTA chelate of copper changes 80–90 mV per 10-fold change in chelate concentration over the range 10^{-2}–$10^{-4}M$. The relationship is almost linear, *cf* Fig. 1.

Thus a controlled concentration of chelate solution must be obtained for polarography. It proved most convenient to control the addition of the copper sulphate solution to the electrophoresis paper; excess complexone was, of course, necessary to ensure migration of all the copper as chelate. An excess of complexone also modifies the value of the half-wave potential of the chelate wave, but fortunately the excess is separated from the copper chelate by the electrophoresis. The whole range of complexone/copper chelates were isolated individually on paper to simulate experimental conditions, and then eluted. During elution the residual buffer from the electrophoresis electrolyte went into solution thus raising the pH of the final solution on which the polarogram was determined to *ca* 2·8. The $E_{\frac{1}{2}}$ values obtained are listed in Table I; the accuracy is ±20 mV. As the DHEG/Cu^{II} did not appear on our pherograms, we used IDA/Cu^{II} ($E_{\frac{1}{2}} = 0$, $\log K = 10{\cdot}6$) in this instance to establish an arbitrary zero, in the plot of the measured change in half-wave potential ($\Delta E_{\frac{1}{2}}$) versus the known difference in stability constant ($\Delta \log K$). Some values of log K were obtained from polarographic data.[5]

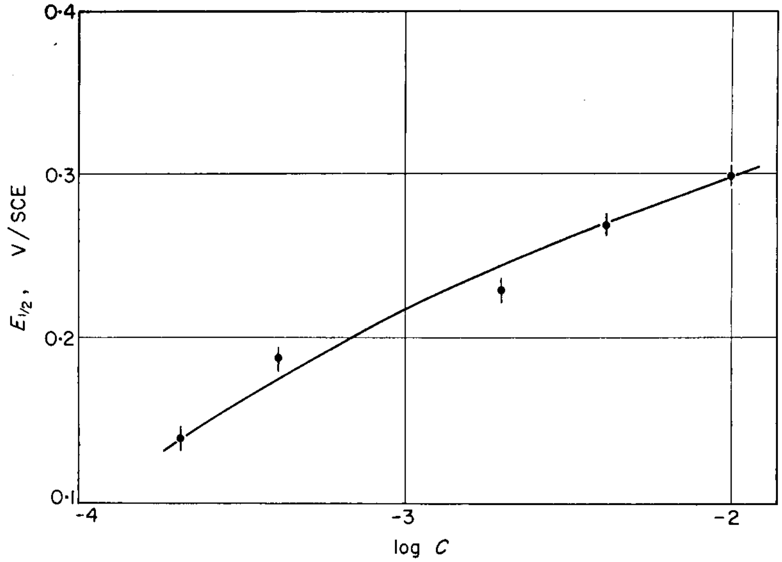

FIG. 1. Variation of $E_{\frac{1}{2}}$ of Cu^{II} chelate of EDTA with concentration. The concentrations of gelatin and acetic acid were kept constant at 0·025% and 0·4M respectively.

The curve produced has a slope almost identical with that obtained from the copper chelates in solution.[5] The use of this curve is restricted to simple complexones, since some complexones with three or more co-ordinating centres behave differently, *e.g.* Chel ME, gives a lower $E_{\frac{1}{2}}$ value and HEEDTA has a much higher $E_{\frac{1}{2}}$ value than expected. It is possible, however, to determine the $\Delta E_{\frac{1}{2}}$ values of new complexones with two co-ordination centres and to obtain the approximate log K value from the graph. In Fig. II the curve has been extrapolated as a straight line beyond the value for CDTA; results obtained from this latter part of the curve must be treated with due caution.

TABLE 1

Group	Complexone	Migration Rates		$E_{\frac{1}{2}}$ Value of Cu^{II} Chelate *mV*	$E_{\frac{1}{2}}$ Value of Cu^{II} Chelate From Pherogram *mV*	$E_{\frac{1}{2}}$ Value of Cd Chelate *mV*
		M_{I_1}	M_{I_2}			
One	DHEG	—	—	0·02	—	
	IDA	1·0		0·06	0·00	0·60
	MIDA	1·2		0·08	0·03	
	UDA*	1·0	2·4	0·16	0·00	
	CHEL 138	1·3		0·16		
		1·8				
	CHEL 138†	Streak	1·5			
Two	HEEDTA	2·6		0·23 (1)	0·22	
	AADA‡	2·7		0·08	0·04	
	CHEL ME*	3·0	1·1	0·10	0·06	
	NTA	3·1		0·11	0·05	0·60
	CHEL DE*	3·2	1·1	0·11	0·06	
Three	CPDTA	3·6		0·24 (1)	0·13	0·93
	CDTA	3·6		0·32 (s)	0·27	1·04
	CHDTA	4·0		0·42	0·37	1·08
	DPTA*	4·0	2·4	0·11	0·07	
	EDTA	4·0		0·23 (s)	0·14	0·82
	DTPA	4·1	2·5	0·21	0·13	
	EDAP	4·2		0·27 (1)	0·18	~
	MEDTA	4·3		0·29 (1)	0·24	0·88
	2:3-BDTA	4·3		0·41 (1)	0·33	0·97

Key to Table

IDA—Iminodiacetic acid
MIDA—Methyliminodiacetic acid
NTA—Nitrilotriacetic acid
UDA—Uramil-N:N-diacetic acid
EDTA—Ethylenediamine-N:N:N′:N′-tetra-acetic acid
MEDTA—1:2-Propanediamine-N:N:N′:N′-tetra-acetic acid
§ EDAP—Ethylenediamine-N:N′-diacetic acid-N:N′-di-β-propionic acid
§ DPTA—1:3-Propanediamine-2-ol-N:N:N′:N′-tetra-acetic acid
DTPA—Diethylenetriamine-N:N:N′:N″:N″-penta-acetic acid
¶ 2:3-BDTA—2:3-Butanediamine-N:N:N′:N′-tetra-acetic acid
DHEG—Di-(2-hydroxyethyl)glycine
AADA—*o*-Carboxyphenyliminodiacetic acid
§ Chel ME—2:2′Bis-[di(carboxymethyl)amino]diethyl ether
§ Chel DE—1:2 Bis-[2-di(carboxymethyl)aminoethoxy]ethane
§ Chel 138—N:N′-Ethylene bis-[2-(*o*-hydroxyphenyl)]glycine
HEEDTA—N-(2-Hydroxyethyl)ethylenediamine-N:N′:N′-triacetic acid
¶ CPDTA—*Cyclo*pentane-*trans*-1:2-diamine-N:N:N′:N′-tetra-acetic acid
CDTA—*Cyclo*hexane-*trans*-1:2-diamine-N:N:N′:N′-tetra-acetic acid
¶ CHDTA—*Cyclo*heptane-*trans*-1:2-diamine-N:N:N′:N′-tetra-acetic acid

* Major migrating species with excess chelating agent is M_{I_1}. (s) and (l) "reversed current" small or large respectively. ~ Not reproducible.

† Excess copper.

‡ Cu^{II} chelate has distinct green-blue colour on the pherogram.

§ Supplied by The Geigy Company Ltd.

¶ Synthesised by the authors.[1,2]

The experimental procedure must be modified for use with mixtures of complexones, since under these conditions it is not possible to control the amount of any particular copper chelate constituent moving along the paper. It should be possible in an identical experiment to ascertain the amount of copper chelate present, from he diffusion current, and in the final determination the concentration of copper chelate in the acetic acid solution may then be adjusted to be comparable with that used to establish the standard curve.

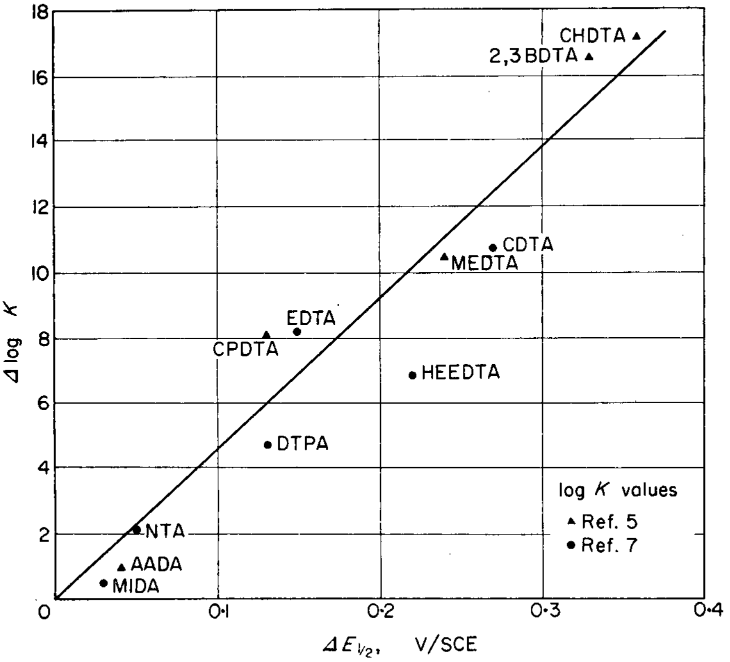

FIG. 2. Variation of $\Delta E_{\frac{1}{2}}$ with Δ log K for complexones isolated from pherograms.

Whilst we have been primarily interested in the evaluation of new complexones, and their intermediates, which are simple analogues of EDTA, we consider the proposed method of direct application to the analysis of complexones both singly and in admixture. The electrophoresis experiment gives a "group" analysis, and within the group most of the individual complexones may be characterised by the half-wave potential of the eluted copper chelate. In a few cases where ambiguous results may be obtained, *e.g.* with EDTA and CPDTA, these complexones can be characterised by the $E_{\frac{1}{2}}$ value of the polarogram of the cadmium chelates, by the colour intensity of the copper chelates or by the nature of the reduction wave.[5] The $E_{\frac{1}{2}}$ values of some Cu^{II} and Cd chelates, the determination of which is described elsewhere,[5] are listed in Table I. Some of these reduction waves exhibited the phenomenon of "reversed current",[5] this is indicated in the Table. The reduction waves of *eluted* copper chelates displayed only a little "reversed current", and it is thought that the phenomenon is a function of the complexone when it is present in excess.

It should prove possible to extend the method to give a quantitative analysis.

EXPERIMENTAL

Paper electrophoresis

Reagents:

pH 5 Buffer: 96 g of hydrated sodium acetate and 17·7 g of glacial acetic acid were dissolved in 1 litre of water, and the solution was made up to 5 litres with distilled water.

Copper sulphate A.R.: 0·2*M* aqueous solution.

Complexone solutions. 0·1*M* aqueous solutions of the sodium salts.

Glucose: 0·2*M* aqueous solution.

Potassium ferrocyanide solution: 2% aqueous solution acidified to the extent of *ca.* 0·1% with concentrated hydrochloric acid before use.

Aniline hydrogen phthalate: 8·3 g of phthalic acid were dissolved in 75 ml. of hot water and 475 ml. of *n*-butyl alcohol; 4·65 g. of aniline were added and the solution was well shaken.

Dithio-oxamide: 0·1% solution in ethanol.

Whatman No. 3 Paper.

Apparatus: The simple type of apparatus used is based on that of Kunkel and Tiselius.[6] A stabilised power-pack capable of giving about 75 ma. at 1000 V d.c. was used. 0·5 ml Agla syringe pipette.

Measurement of migration rates

20 μl of the copper sulphate solution were added to the cathode end of the paper from an Agla syringe in two lots of 10 μl each. About three micro-equivalents each of IDA and the complexone, and one drop of the glucose solution were added. The paper was dried after the addition of each spot. The migration rates of di-carboxylic acid complexones were measured by reference to IDA and glucose on a separate track on the same paper. The paper was soaked in buffer solution, blotted, and clamped tightly between glass plates 45 cm long. A potential of 1000 V was applied to the paper for a period of about 2 hr. After the paper had been dried, the area about the origin was sprayed with the solution of aniline hydrogen phthalate and heated for some minutes to develop the glucose spots. The paper was then sprayed with ferrocyanide solution and again dried by heating. On exposure to light over a period of time the paper becomes discoloured, and is thus best stored in the dark. Alternatively the paper may be sprayed with a solution of dithio-oxamide.

Isolation of known copper chelates for elution and polarographic examination

10 μl of the copper sulphate solution was applied to the paper as above. Excess of complexone was added and each spot was dried before the addition of the next. Electrophoresis was carried out as before, the paper was dried, and the spots later removed for polarography.

The qualitative analysis of simple complexone mixtures

The mixture of complexones or reaction liquor containing complexones and intermediates was spotted on the paper, and excess copper sulphate solution was added. Electrophoresis was carried out as described above, and the paper was sprayed with ferrocyanide solution. The migration rates of new complexones containing three or more carboxylic acid groups were determined by reference to IDA and glucose on the same track; when dealing with mono- and di- acids the IDA reference spot was run on a separate track on the same paper. In a subsequent experiment the quantities of reagents were adjusted where possible to give spots of the copper chelates containing the equivalent of 10 μl of 0·2*M* $\mathrm{Cu^{II}}$ solution, which were removed, eluted and examined polarographically.

Polarography

Reagents:

Acetic acid solution: 0·8*M* Aqueous solution containing—

Gelatin: 0·05% freshly prepared before use.

Apparatus:

Tinsley Recording Polarograph Mark 19, with dropping mercury electrode (drop time 5·2 sec, under an open head of mercury of 37 cm) and a saturated calomel electrode with a potassium chloride bridge as a reference electrode. E.I.L. Direct Reading pH Meter.

The polarographic examination of eluted pherograms

The copper chelates separated by electrophoresis were cut out from the paper and placed in 5 ml of distilled water in a 20-ml beaker, and allowed to stand for thirty minutes with occasional stirring. 5 Ml of the 0·8*M* acetic acid solution were then added and the paper was removed from the beaker. The pH of the solution was measured (to ensure that it was 2·8 ± 0·1) and the solution was then polarographed, using a damping of 1, a counter current of 2, a sensitivity of 1·5 μA, and a chart scale of 1 V/4″. The half-wave potentials were measured from the curve drawn through the points given by the current at maximum *drop* size.

The polarographic determination of Cu^{II} and Cd chelate stabilities has been described elsewhere.[5]

Acknowledgement—We are grateful to the Geigy Company, Ltd., for supplying certain of the samples used and for the provision of a research grant to one of us (W. H.). We also wish to record our thanks to Professor R. Belcher and Dr. A. B. Foster of this Department for their interest and helpful advice.

Zusammenfassung—Eine Methode zur Unterscheidung verschiedener Polyamincarboxysäuren (Komplexone) durch Papierelektrophorese ihrer Kupferchelate bei pH 5 wird beschrieben. Die getrennten Chelate werden vom Pherogram gelöst und in 0,4 n Essigsäure polarographisch untersucht. Wanderungsgeschwindigkeiten werden in einigen Fällen mitgeteilt. Diese, sowie das Halbstufenpotential sind manchmal zur Charakterisierung des Komplexons ausreichend. Durch Anwendung einer Eichkurve kann auf Grund bekannter Beziehungen zwischen $E_{1/2}$ und log *K*-werten eine grobe Abschätzung der Stabilität der Kupferchelate erfolgen.

Résumé—Une méthode permettant de différencier divers types d'acides polyaminocarboxyliques (complexons) par électrophorèse sur papier de leurs chelates cuivriques à pH 5 est décrite; quelques vitesses de migration sont indiquées. Les chelates ainsi séparés peuvent être rédissous du pherogramme et étudiés par polarographie dans l'acide acétique 0,4 *M*. Dans beaucoup de cas les valuers de $E_{1/2}$ et la vitesse de migration électrophorétique (M_I) sont utilisées pour caractériser le complexon. Par l'emploi d'une courbe d'étalonnage reliant les valeurs de $E_{1/2}$ observées aux valeurs connues de log *K*, on peut obtenir une estimation de la stabilité du chelate de cuivre.

REFERENCES

[1] W. Hoyle, M.Sc. Thesis, Birmingham, 1957.
[2] R. Belcher, W. Hoyle and T. S. West, Unpublished work.
[3] K. Macek and R. Přibil, *Coll. Czech. Chem. Comm.*, 1955, **20**, 715.
[4] D. Betteridge and W. Hoyle, Unpublished work.
[5] W. Hoyle and T. S. West, *Talanta*, 1959, **2**, 158.
[6] H. G. Kunkel and A. Tiselius, *J. Gen. Physiol.*, 1951, **35**, 89; R. P. Linstead, J. A. Elvidge and M. Whalley, *A Course in Modern Techniques of Organic Chemistry*, Butterworths, London, 1955; A. B. Foster, Private Communication.
[7] *Stability Constants, Part I, Organic Ligands, Chem. Soc.* Special Publication No. 6, 1959.

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UNTERSUCHUNG EINIGER ALS REDOXINDICATOREN ANWENDBAREN VARIAMINBLAUDERIVATEN

L. Erdey, É. Bányai und É. B.-Gere
Aus dem Institut für Allgemeine Chemie der Technischen Universität, Budapest, Ungarn

Zusammenfassung—Es wurde über die ausführliche elektrochemische Untersuchung der als Indicatoren verwendbaren mit verschiedenen elektrophylen und nukleophylen Gruppen substituierten Derivate des 4-Amino-4′-methoxy-diphenylamins (Variaminblau) berichtet. Der reversible Redoxvorgang dieser Verbindungen ist zweielektronig, ihr Oxydationsmechanismus entspricht dem des Variaminblaus, d.h. ihre oxydierte Form entspricht dem entsprechend substituierten Derivat des Chinon-p-anisil-diimins. Bei der Oxydation des 2-Methyl- und 2-Methoxyproduktes entsteht auch ein intermediäres semichinoidales Oxydationsprodukt. Die Instabilität der Systeme in saurer Lösung ist durch den Zerfall der oxydierten Form verursacht. Mit Hilfe der Elektrodengleichungen können die Redoxpotentiale für beliebigen pH-Wert berechnet werden. Die Brechpunkte der E_0'-pH-Kurven geben die Säure-Basendissociationskonstanten der oxydierten und reduzierten Formen. Nukleophyle Substituenten erhöhen, elektrophyle Substituenten erniedrigen die Basicität des Variaminblaumoleküls.

Die ausgezeichneten Eigenschaften des Variaminblaus /4-Amino-4′-methoxy-diphenylamin/ als Redoxindicator[1–21] und als colorimetrisches Reagens[22–27] gaben uns den Gedanken seine verschieden substituierten Derivate herzustellen.[28,29] Es war zu erwarten, dass diese Derivate sich als Redoxindicatoren ebenfalls gut bewähren und dass sie ein von der Grundverbindung abweichendes Umschlagspotential besitzen werden. Die Untersuchungen von Fieser und Thompson,[30] Fieser und Fieser[31] und anderen[32] zeigten, dass elektrophyle Substituenten das Redoxpotential der Grundverbindung in positive, nukleophyle Substituenten dagegen in negative Richtung verschieben. Ähnliche Potentialverschiebung beobachteten auch wir im Falle einiger Derivate des Variaminblaus, wie darüber schon berichtet wurde.[29] Im folgenden werden die Ergebnisse der ausführlichen physico-chemischen Untersuchung der als Redoxindicatoren verwendbaren Derivate des Variaminblaus mitgeteilt. Diese Versuche breiteten sich auf die Bestimmung der Funktion Redoxpotential-pH, der Zahl der im Vorgang beteiligten Elektronen, der Säure-Basendissociationskonstanten der reduzierten und oxydierten Formen aus. Es wurde weiterhin die Reversibilität der Vorgänge und die Möglichkeit der Bildung von intermediären Produkten untersucht.

EXPERIMENTELLER TEIL

Die Redoxpotentiale wurden teilweise polarographisch, teilweise potentiometrisch bestimmt. Die polarographischen Messungen wurden mit einem Polarograph Typ Heyrovsky V 301 im Kalousek-Gefäss unter Anwendung einer tropfenden Quecksilberelektrode und einer Quecksilber (I) sulphatvergleichselektrode in Stickstoffatmosphäre durchgeführt. Die Elektroden wurden anodisch-kathodisch polarisiert. Die Quecksilberniveauhöhe (h) betrug 50 cm. Die Daten der angewandten Kapillare waren: $m = 7{,}2$ mg/s, $t = 1{,}84$ s. Die zur Untersuchung von instabilen Systemen sehr geeignete schnelle polarographische Methode ersetzten wir nur dann mit einer potentiometrischen, wenn unter den gegebenen Verhältnissen keine Stufe erhalten werden konnte. Die potentiometrischen Titrationen erfolgten ebenfalls in Stickstoffatmosphäre zwischen einer Indicatorenelektrode aus Platin und einer Vergleichselektrode aus gesättigtem Kalomel. Zur Oxydation diente in saurer Lösung 0,01 n

Bromwasser, in alkalischer Lösung ausserdem noch eine 0,01 n Kaliumhexacyanoferrat(III)lösung. Bei instabilen Systemen wurde nach der stufenweisen Methode gearbeitet.[29]

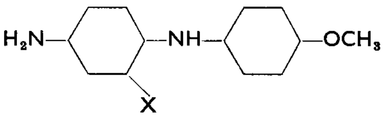
Die optischen Messungen—u.zw. die Aufnahme der Absorptionskurven und der Zusammenhänge zwischen Extinktionskoeffizient und pH zur Bestimmung der Säure-Basendissociationskonstanten der farbigen oxydierten Formen[33,34]-wurden mit Hilfe des Pulfrich Photometers unternommen.

Über die Erzeugung der Indicatoren berichteten wir schon vorangehend.[29] Die 2-Amino, 2-Methyl- und 2-Methoxyderivate wurden in 0,005 m alkoholischer, die 2-Sulfonsäurederivate in 0,001 m schwach alkalischer, das 2-Carbonsäureanilid in 0,0025 m schwach saurer Lösung benützt in Pufferlösungen gemäss Britton-Robinson.[35] Die pH-Messungen wurden mit Wasserstoffelektrode durchgeführt.

ALLGEMEINE CHARAKTERISIERUNG DER INDICATOREN

Das Verhalten folgender Indicatoren wurde näher untersucht:

Generalformel:



I. 4-Amino-4′-methoxy-diphenylamin (Variaminblau)

$X = -H$

II. 2,4-Diamino-4′-methoxy-diphenylamin

$X = -NH_2$

III. 4-Amino-2,4′-dimethoxy-diphenylamin

$X = -OCH_3$

IV. 4-Amino-2-methyl-4′-methoxy-diphenylamin

$X = -CH_3$

V. 4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure

$X = -SO_3H$

VI. 4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure-anilid

$X = -SO_2-NH-C_6H_5$

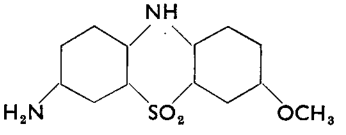
VII. 4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure-anisidid

$X = -SO_2-NH-C_6H_4-OCH_3$

VIII. 4-Amino-4′-methoxy-diphenylamin-2-sulfonsaurer Methylester

$X = -SO_3CH_3$

IX. 2-Amino-7-methoxy-phenthiazin-9-dioxyd



X. 4-Amino-4′-methoxy-diphenylamin-2-carbonsäure-anilid

$X = -CO-NH-C_6H_5$

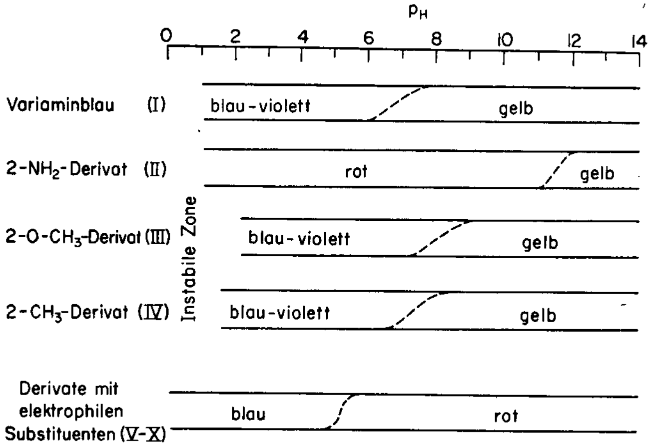
XI. Variaminblau-pikrat

1 Mol Variaminblau + 2 Mol Pikrinsäure

Die Oxydation der in Leukoform leicht präparierbaren farblosen, oder schwach gelblichgrünen Verbindungen ist mit einer intensiven Farbänderung verbunden, worüber Tab. I. eine Übersicht gibt.

In saurem Medium färbt sich die wässrige oder alkoholische Lösung des Variaminblau (I), der 2-Methoxy (III) und 2-Methyl (IV) Derivate auf Einwirkung einer geringfügigen Menge an Oxydationsmittel auf blau. Die Farbe der Holochinone* ist violett. Das Absorptionsmaximum des blauen Oxydationsproduktes fällt zwischen 570–610 $m\mu$, während das der Holochinone gegen die kürzeren Wellenlängen verschoben ist. Auf Einwirkung von überschüssigen starken Oxydationsmitteln entsteht ein rotes Oxydationsprodukt. In alkalischem Medium kommt nur ein gelbes Oxydationsprodukt zustande. Die Holochinone des 2-Aminoderivates (II) sind rot und gelb. Die in saurem Medium beobachtbare blaue Färbung verschwindet augenblicklich. Die Holochinone der 2-Sulphonsäuregruppe (V–IX) und des Variaminblau-2-carbonsäureanilids (X) sind blau und rot. In den mit S-förmigen Kurven bezeichneten pH-Intervallen bilden sich die Mischfarben der aufgezählten sauren und alkalischen Grenzfarben aus.

TABELLE I



Die nukleophyle Substituenten enthaltenden Leukoderivate (II–IV) geben im pH-Bereich 3–14 gut auswertbare anodische polarographische Oxydationsstufen. Bei niedrigeren pH-Werten als 3 wirkt die anodische Auflösung des Quecksilbers auf die Ausbildung der Stufen störend ein. Die Stufenhöhen sind mit der Konzentration und $\sqrt{h}$ direkt proportional, d.h. es handelt sich hier um Diffusionsstufen. Von den mit elektrophylen Gruppen substituierten Derivaten geben die Mitglieder der Variaminblau-2-sulphonsäuregruppe (V–IX) nur in stark alkalischem Medium eine polarographische Stufe, das Variaminblau-2- carbonsäureanilid (X) ist polarographisch inaktiv.

ZAHL DER IM REDOXVORGANG BETEILIGTEN ELEKTRONEN, REVERSIBILITÄT UND OXYDATIONSMECHANISMUS

Die Äquivalenzpunkte der oxydimetrischen potentiometrischen Titrationen deuteten ähnlich dem Variaminblau auf einen zweielektronigen Redoxvorgang.[1,28,36,37] Mit voller Sicherheit konnte man diese Frage jedoch nur auf polarographische Weise entscheiden. In gleicher Konzentration stimmt die Höhe der anodischen Oxydationsstufe des Leukovariaminblaus und dessen Derivate miteinander beinahe überein (Abb. 1,2). Der ungefähr 30 mV betragende Neigungswinkel der durch mathematische Analyse der polarographischen Stufen erhaltenen log $(i/i_d - i) - V$ Funktionen weist ebenfalls auf einen zweielektronigen Redoxvorgang. Mit den nukleophylen Substituenten enthaltenden Derivaten, die gut auswertbare Stufen geben, wurden auch polarometrischen Titrationen unternommen; der Äquivalenzpunkt der Titrationen der Leukofarbstoffe entspricht ebenfalls einer zweielektronigen Oxydation (Abb. 3).

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* Unter Holochinon verstehen wir diejenige oxydierte Form, die auf Einwirkung von einer zweielektronigen Oxydation entsprechenden Mengen des Oxydationsmittels entsteht.

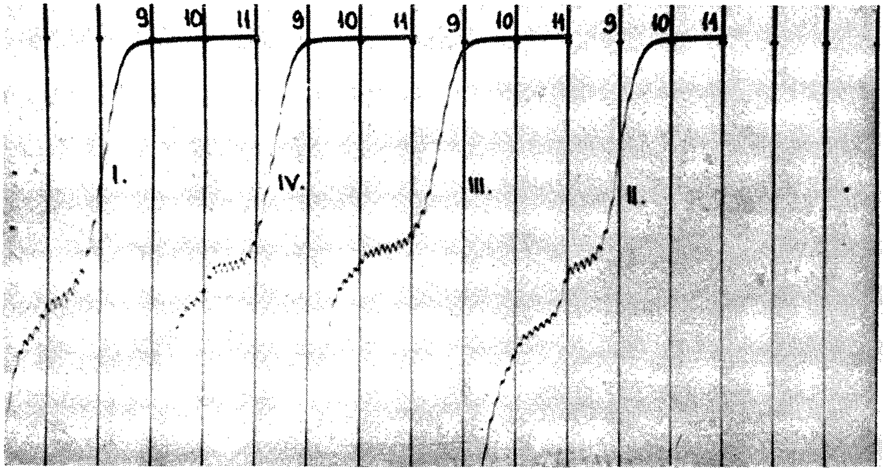


ABB. 1. Vergleich der polarographischen Stufenhöhen von Variaminblau und seiner nukleophyle Substituenten enthaltenden Derivate. Variaminblau (I), 2-Methyl derivat (IV), -2-Methoxyderivat (III), 2-Aminoderivat (II). Farbstoffkonzentration $= 5 \cdot 10^{-4}$ Mol/Liter. pH $= 9{,}5$. 100 mV/Absc., Empf. 1/20.

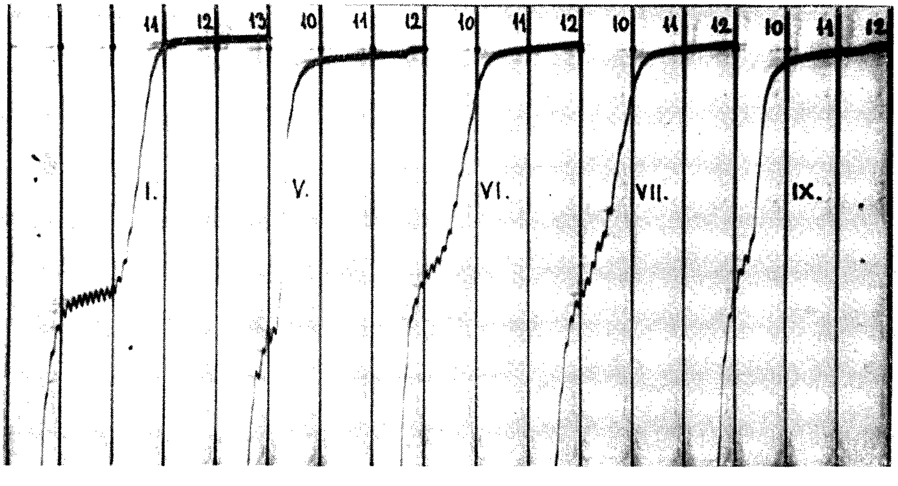


ABB. 2. Vergleich der polarographischen Stufenhöhen von Variaminblau und seiner elektrophyle Substituenten enthaltenden Derivate. Variaminblau (I), Variaminblau-2-sulfonsäure (V), Variaminblau-2-sulfonsäure-anilid (VI), Variaminblau-2-sulfonsäure-anisidid (VII) und 2-Amino-7-methoxy-phenthiazin-9-dioxyd (IX). Farbstoffkonzentration: $3{,}3 \cdot 10^{-4}$ Mol/l. pH $= 13{,}5$, 100 mV/Absc., Empf. 1/15.

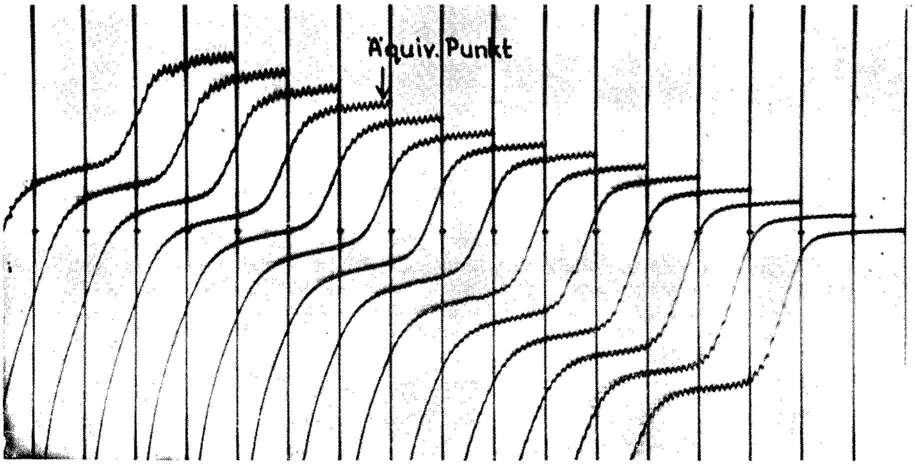
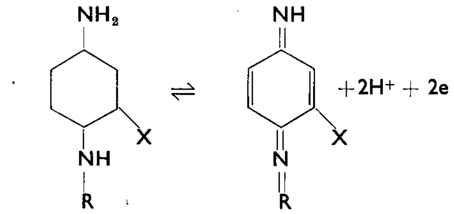


Abb. 3. Polarometrische Titration des 2,4-Diamino-4′-methoxy-diphenylamins (II). Anfangskonzentration = $1 \cdot 10^{-4}$ Mol/liter, pH = 4,6, die Kurven sind vom 10. Draht rückwärts aufgenommen, Oxydationsmittel: 0,01 n Kaliumhexacyanoferrat(III)-lösung, 100 mV/Absc., Empf. 1/30.

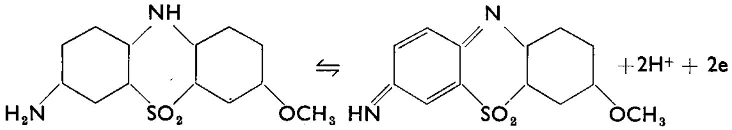
Die Reversibilität der Redoxvorgänge ist in erster Linie durch die Linearität des erwähnten log $(i/i_d - i) - V$ Zusammenhanges bewiesen. Das Halbstufenpotential der anodischen Oxydationsstufe der mit nukleophylen Gruppen substituierten Derivate stimmt mit dem Halbstufenpotential der kathodischen Reduktionsstufe der in der Lösung oxydierten Formen gut überein. Im Falle von Verbindungen mit elektrophylen Substituenten konnte man diese Identität nicht nachweisen. Die potentiometrischen Untersuchungen, weiterhin die mathematische Analyse der anodischen Oxydationsstufen weisen aber auch in diesem Falle eindeutig auf einen reversibilen Redoxvorgang.

Ähnlich dem Variaminblau lässt sich auch für die substituierten Produkte folgender potentialbestimmender Vorgang aufschreiben:



$R = -C_6H_4-OCH_3$ $X =$ Substituent

Im Falle von 2-Amino-7-methoxy-phenthiazin-9-dioxyd (IX) ändert er sich folgendermassen:



Wir können also auch ohne jegliche präparative Beweise behaupten, dass die vollständig oxydierten Formen (Holochinone) der Derivate nur dem Chinon-p-anisil-diimin entsprechende substituierte bzw. ringgeschlossene Produkte sein können.

Die Oxydation des 2-Methyl-(IV) und des 2-Methoxyproduktes (III) verläuft in saurer Lösung bis pH-Wert 6 ähnlich dem Variaminblau unter Bildung eines intermediären semichinoidalen Oxydationsproduktes. Die vom Holochinon abweichende Farbe des im geringen Masse oxydierten Farbstoffes und die mehr als 14 mV betragenden Indexpotentiale der Titrationskurven zeigen ebenfalls, dass hier ein Semichinon zustandekommt.[38] Die Index-potentiale sind innerhalb der Konzentrationen $1 \cdot 10^{-3}$–$2 \cdot 10^{-4}$ Mol/Liter von der Farbstoffkonzentration unabhängig, das Übergangsprodukt besteht folglich aus freien Radikalen. Die aus freien Radikalen bestehende Struktur wird durch die Zahl der mesomeren Möglichkeiten stabilisiert. In Tab. II sind die charakteristischen Daten der Semichinonbildung dargelegt.

Im Falle von elektrophylen Substituenten wurde keine Semichinonbildung beobachtet (V–X). Die elektrophylen Substituenten üben hier wahrscheinlich eine Anziehung auf das einsame Elektron der aus freien Radikalen bestehenden Struktur aus, wodurch die Zahl der mesomeren Möglichkeiten abnimmt, deshalb die Stabilität der Struktur aufhört.

Die auf Einwirkung des überschüssigen Chlor- und Bromwassers entstehende rote Verbindung ist ein zerstörtes Oxydationsprodukt. Die aus der konzentrierten

Lösung des Variaminblau-2-carbonsäureanilid (X) präparierte dunkelviolette Verbindung löst sich in Alkohol mit roter Farbe, wirkt oxydierend und färbt die Lösung des Leukofarbstoffes blau. Laut Analysenergebnisse enthält diese Verbindung keine Halogene und ihr 2,85%-iger Stickstoffgehalt ist wesentlich geringer als der des Holochinons.

Die in die Variaminblaureihe gehörenden Redoxsysteme zeigen ebenfalls die der Diamin-diiminsysteme typisch eigene Instabilität, die in erster Linie durch den Zerfall der oxydierten Form verursacht wird.[39–41]

TABELLE II

Verbindungen	$E_{i\ 25\%}$ mV 20°C	k	$(s/a)_{max}$
4-Amino-2,4′-dimethoxy-diphenylamin (III)	16	$8{,}4 \cdot 10^{-2}$	0,12
4-Amino-2-methyl-4′-methoxy-diphenylamin (IV)	15	$2{,}9 \cdot 10^{-2}$	0,07

E_i = Indexpotential
k = Semichinonbildungskonstante
$(s/a)_{max}$ = Maximale Menge des entstandenen Semichinons im Verhältn zuris Gesamtfarbstoffkonzentration.

Laut unserer polarographischen Untersuchungen zerfallen die Holochinone der verschiedenen Derivate sogar in Stickstoffstrom, wobei teilweise Zersetzungprodukte mit negativeren Halbstufenpotentialen entstehen. Die Potentialstabilität der halboxydierten Indicatorsysteme ist ebenfalls veränderlich. Die Zersetzung der oxydierten Formen geht mit Farbänderung vor sich, sodass dieser Erscheinung bei der praktischen Anwendung der Indicatoren eine bedeutende Rolle zukommt. Mass und Geschwindigkeit der Zersetzung ist vom pH und von dem Substituenten selber abhängig. In einem mittelmässig sauren Medium (pH $\sim$ 2–6) ändert sich das Potential und damit die Farbe der halboxydierten Systeme des Variaminblau (I), der 2-Methoxy- (III) und 2-Methyl- (IV) derivate nur kaum, was mit dem Entstehen stabiler semichinoidaler Radikale sich erklären lässt. Die in stark saurem Medium ($pH < 2$) beobachtbare, mit einer raschen Entfärbung verbundene Zersetzung lässt sich wahrscheinlich auf die Hydrolyse des chinondiiminartigen Moleküls auf Chinon und Ammoniak zurückführen. Im Laufe von in saurem Medium durchgeführter Farbstoffoxydation gelang es tatsächlich nach einer gewissen Zeitdauer in der Lösung NH_4^+ Ionen nachzuweisen. Es ist möglich, dass dieser Vorgang durch die bei niedrigeren pH-Werten erfolgende zweite Protonenaufnahme des Moleküls gefördert wird, da die dadurch entstehende, aufgelockerte Struktur des Moleküls die Substitution der $=NH_2^+$- Gruppe auf $=OH^+$-Gruppe ermöglicht. Die Potentiale der elektrophyle Substituente enthaltenden Derivate (V–X) nehmen mit der Zeit allmählich ab u.zw. mit der vom pH abhängigen Geschwindigkeit linear. Der Potentialfall wird vom allmählichen Verblassen der blauen Farbe begleitet. Diese Verbindungen lassen sich im pH-Bereich 2–5 als Indicatoren anwenden.

REDOXPOTENTIAL-pH FUNKTIONEN

Im Sinne des Oxydationsmechanismus ist das Redoxpotential der Indicatorsysteme pH-abhängig. Die erhaltenen Ergebnisse sind in Abb. 4 und 5 graphisch dargestellt. Die Kurve E_0'-pH der Mitglieder der Variaminblau-2-sulphonsäuregruppe (V-IX) konnten nur im pH-Bereich 1–7 ermittelt werden. In mehr alkalischem Medium zufolge der Instabilität dieser Systeme können nämlich sogar mit Hilfe der stufenweisen potentiometrischen Methode keine verlässlichen Ergebnisse erzielt werden. Im Falle des Variaminblau-2-carbonsäureanilids (X) konnte der Zusammenhang nur bis pH ∼5 festgestellt werden, da schon bei pH = 4,7 die freie Base der reduzierten Form selbst in dünnen Lösungen auszuscheiden beginnt. Das Verhalten des Variaminblaupikrats in saurem Medium stimmt mit dem des Variaminblaus überein.

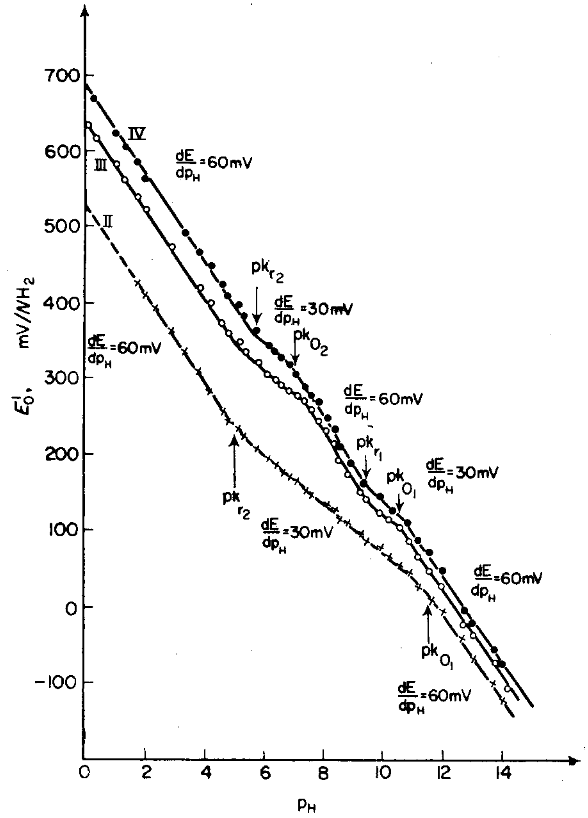


Abb. 4. E_0'-pH-Kurven der nukleophyle Substituenten enthaltenden Derivate. 4-Amino-2-methyl-4'-methoxy-diphenylamin (IV), 4-Amino-2,4'-dimethoxy-diphenylamin (III), 2,4-Diamino-4'-methoxy-diphenylamin (II).

Die durch die linearen Strecken mit verschiedenen Neigungswinkeln der E_0'-pH Kurven gegebenen Knickpunkte entsprechen den Säure-Basendissociationskonstanten der reduzierten und oxydierten Formen. Im Falle der Variaminblau-2- sulphonsäure (V) wurde keine bajonettartige Knickung beobachtet, was dem kleinen Unterschied zwischen pK_0 und pK_r zuzuschreiben ist. Auf optischem Wege ergab sich der pK_0-Wert zu 4,1. Die Dissociationskonstanten der mit Farbänderung verbundenen

Protonenabgabe der oxydierten Formen wurden auch bei den übrigen Derivaten auf optischem Wege kontrolliert. Die erhaltenen Werte stimmen mit den durch die entsprechenden Knickpunkte dargestellten Werten gut überein. Die Grössenordnung einiger Werte wurde auf qualitativem Wege bewiesen. So z.B. die Farbänderung der oxydierten Form des 2-Aminoderivates (II) erfolgt in stark alkalischem Medium in der Nähe des beobachteten Knickpunktes; die pK_{r1} -Werte der 2-Methoxy (III) und 2-Methyl (IV) Derivate müssen höher sein als die Konstante des Variaminblaus, weil in der Lösung ihrer salzsauren Salze die Ausscheidung der freien Base auf die Zugabe von grösserer Laugenmengen beginnt als im Falle des Variaminblaus.

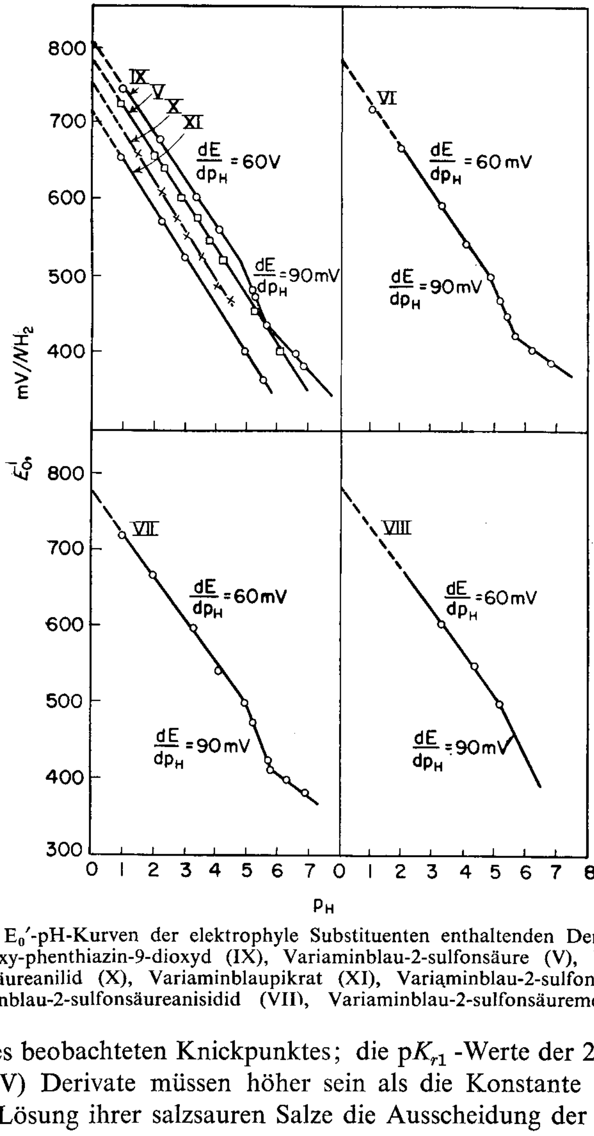


Abb. 5. E_0'-pH-Kurven der elektrophyle Substituenten enthaltenden Derivate. 2-Amino-7-methoxy-phenthiazin-9-dioxyd (IX), Variaminblau-2-sulfonsäure (V), Variambinblau-2-carbonsäureanilid (X), Variaminblaupikrat (XI), Variaminblau-2-sulfonsäureanilid (VI), Variaminblau-2-sulfonsäureanisidid (VII), Variaminblau-2-sulfonsäuremethylester (VIII).

Die Elektrodengleichung der untersuchten Derivate hat folgende Formel:

$$E = E_0 + 30 \log \frac{[\mathrm{ox}]t}{[\mathrm{red}]_t} + 30 \log \frac{K_{r1}K_{r2} + K_{r2}[H^+] + [H^+]^2}{K_{01}K_{02} + K_{02}[H^+] + [H^+]^2} - 60 \text{ pH} \quad \text{bei } 30°\text{C}$$

Beim 2-Aminoprodukt (II) und bei den 2-Sulfonsäureverbindungen (V–IX), wo die

Gültigkeit der Gleichung versuchsmässig nur zwischen den pH-Werten 0 und 7 bewiesen werden konnte, lässt sich diese Gleichung vereinfacht schreiben:

$$E = E_0 + 30 \log \frac{[\mathrm{ox}]_t}{[\mathrm{red}]_t} + 30 \log \frac{K_r + [H^+]}{K_0 + [H^+]} - 60\ \mathrm{pH} \quad \text{bei } 30°\mathrm{C}$$

Das Redoxpotential des Variaminblau-2-carbonsäure-anilids (X) und des Variaminblaupikrats (XI) ändert im pH-Gebiet 0–5 je ein pH-Wert mit 60 mV:

$$E = E_0 + 30 \log \frac{[\mathrm{ox}]_t}{[\mathrm{red}]_t} - 60\ \mathrm{pH} \quad \text{bei } 30°\mathrm{C}$$

Die Dissociationskonstanten der Gleichungen sind Dissociationskonstanten gemäss der Brönstedschen Theorie aus welchen die üblichen basischen Dissociationskonstanten mit Hilfe des Ausdrucks

$$K_r \cdot K_{br} = 10^{-14} \quad \text{bzw. } pK_r + p_{br} = 14$$

ermittelt werden können. Die Dissociationskonstanten sind also folgendermassen definiiert:

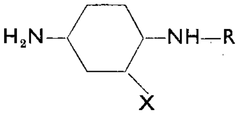
$$\mathrm{red\ H_2^{++}} \leftrightharpoons \mathrm{red\ H^+} + \mathrm{H^+} \qquad K_{r2} = \frac{[\mathrm{red\ H^+}] \cdot [\mathrm{H^+}]}{[\mathrm{red\ H_2^{++}}]}$$

$$\mathrm{red\ H^+} \leftrightharpoons \mathrm{red} + \mathrm{H^+} \qquad K_{r1}K_r = \frac{[\mathrm{red}] \cdot [\mathrm{H^+}]}{[\mathrm{red\ H^+}]}$$

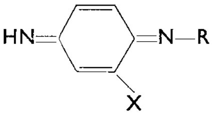
$$\mathrm{ox\ H_2^{++}} \leftrightharpoons \mathrm{ox\ H^+} + \mathrm{H^+} \qquad K_{02} = \frac{[\mathrm{oxH^+}] \cdot [\mathrm{H^+}]}{[\mathrm{ox\ H_2^{++}}]}$$

$$\mathrm{ox\ H^+} \leftrightharpoons \mathrm{ox} + \mathrm{H^+} \qquad K_{01}K_0 = \frac{[\mathrm{ox}] \cdot [\mathrm{H^+}]}{[\mathrm{ox\ H^+}]}$$

red =



ox =



Die charakteristischen elektrochemischen Daten der Derivate u.zw. die Redoxnormalpotentiale und die Dissociationskonstanten der reduzierten und oxydierten Formen sind in Tab. III. zusammengestellt. Die E_0-Werte sind aus den in mässig sauren Lösungen erhaltenen linearen Zusammenhangen extrapolierte Werte. Die mit * bezeichneten pK_0-Werte sind Mittelwerte der durch die Brechpunkte gegebenen und auf optischem Wege erhaltenen Ergebnisse oder auf rein optischem Wege ermittelte Werte.

Wie es aus der Tabelle ersichtlich ist, gestalten nukleophyle Gruppen die Grundmolekel basischer. Infolge der Zunahme der Elektronendichte ist das einsame Elektronenpaar der Stickstoffatome durch den aromatischen Ring weniger in Anspruch genommen, so, dass die Protonenaufnahme auch schon in weniger saurer Lösung erfolgen kann. Der Zusammenhang zwischen den nukleophylen Charakter und der Zunahme der Basicität kann besonders gut bei den Dissociationskonstanten der oxydierten Formen beobachtet werden. Die elektrophylen Substituenten erniedrigen

TABELLE III

Verbindungen	E_0 mV/n H_2 pH = 0	pK_{r1}	pK_{r2}	pK_{o1}	pK_{o2}
2,4-Diamino-4′-methoxy-diphenylamin (II)	532	kein Brechpunkt	5,0	11,5	kein Brechpunkt
4-Amino-2,4′-dimethoxy-diphenylamin (III)	636	9,6	5,2	10,6	7,5*
4-Amino-2-methyl-4′-methoxy-diphenylamin IV	686	9,4	5,7	10,5	7,0*
4-Amino-4′-methoxy-diphenylamin (I)	712	5,9	unmessbar	6,6	unmessbar
4-Amino-4′-methoxy-diphenylamin-2-carbonsäure-anilid (X)	754	≈4,7	unmessbar	≈5,5*	unmessbar
4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure (V)	776	—	unmessbar	4,1*	unmessbar
4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure-anisidid (VII)	780	5,9	unmessbar	5,0	unmessbar
4-Amino-4′-methoxy-diphenylamin-2-sulfonsaurer Methylester (VIII)	786	—	unmessbar	5,1	unmessbar
4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure-anilid (VI)	788	5,7	unmessbar	4,7	unmessbar
2-Amino-7-methoxy-phenthiazin-9-dioxyd (IX)	800	5,8	unmessbar	4,7	unmessbar

aus demselben Grund die Basicität der Grundmolekel. Die mit mehreren Grössenordnungen erfolgende Änderung der Basicität weist darauf, dass hier nicht nur polare, sondern auch sterische Effekte zur Rolle kommen. Die pK_r und pK_0 Werte der Glieder der 2-Sulfonsäuregruppe (V–IX) ändern untereinander kaum. Dies beweist, dass die auf den aromatischen Ring ausgeübte elektrophyle Wirkung der Sulfonsäuregruppe durch weitere Bindungen ausser dem Kern mehr kaum beeinträchtigt wird.

Verfasser danken Frau I. Kucsera und M. Tésy, weiterhin Herrn T. Meisel für die Mithilfe bei den Untersuchungen.

Summary—A report is presented of a detailed electrochemical investigation of substituted derivatives of 4-amino-4′-methoxydiphenylamine (Variamin Blue) as indicators for use with different electrophilic and nucleophilic groups. The reversible "redox" process of these compounds corresponds to two electrons, and their oxidation mechanism corresponds to that of Variamin Blue, *i.e.*, their oxidised form corresponds to the correspondingly substituted derivative of quinone-*p*-anisil-di-imine. In the oxidation of 2-methyl- and 2-methoxy-products an intermediate semi-quinoidal oxidation product also occurs. The instability of the system in acid solution is brought about by the decomposition of the oxidised form. By means of electrode equations the "redox" potentials at desired pH values can be calculated. The point of inflection of the E_0'-pH curves gives the acid-base dissociation constants of the oxidised and reduced forms. Nucleophilic substituents raise, and electrophilic substituents lower the basicity of the Variamin Blue molecules.

Résumé—Les auteurs présentent une étude électrochimique détaillée des dérivés substitués de l'amino-4 méthoxy-4′ diphénylamine (blue de variamine), dérivés utilisés comme indicateurs et comportant différents groupements électophiles et nucléophiles. Le comportement reversible du point de vue oxydo-réduction, de ces composés correspond à l'échange de deux électrons et le mécanisme de leur oxydation correspond à celui du bleu de variamine, c'est à dire que les formes oxydées de ces dérives correspondent aux dérivés substitués correspondants de la p.anisil di-imine-quinone. Dans l'oxydation des composés méthyl-2 et méthoxy-2, on obtient aussi un produit d'oxydation semi-quinonique intermédiaire. L'instabilité du système en solution acide est due à la décomposition de la forme oxydée. Au moyen d'équations relatives aux phénomènes aux électrodes, les potentiels "redox" pour différents pH ont été calculés. Le point d'inflection des courbes E_0'-pH fournit les constantes de dissociation des formes oxydées et réduites. Les substituants nucléophiles augmentent le caractère basique des molécules de bleu de variamine, alors que les substituants électrophiles le diminuent.

LITERATUR

[1] L. Erdey u. A. Bodor, *Z. analyt. Chem.*, 1953, **137,** 410.
[2] L. Erdey, E. Bodor u. M. Pápay, *Acta Chim. Hung.*, 1955, **5,** 235.
[3] L. Erdey, F. Szabadváry, *ibid.*, 1954, **4,** 325.
[4] L. Erdey u. I. Buzás, *ibid.*, 195.
[5] *Idem, ibid.*, 1956, **8,** 263.
[6] L. Erdey u. L. Pólos, *Z. analyt. Chem.*, 1956, **153,** 411.
[7] Z. Jach, J. Pacovsky u. M. Svach, *ibid.*, 1957, **154,** 185.
[8] L. Erdey, E. Bodor u. I. Buzás, *Acta Chim. Hung.*, 1955, **7,** 277.
[9] *Idem, ibid.*, 287.
[10] L. Erdey, K. Vigh u. E. Bodor, *ibid.*, 293.
[11] L. Erdey u. K. Vigh, *Z. analyt. Chem.*, 1957, **157,** 184.
[12] L. Erdey u. L. Káplár, *ibid.*, 1958, **162,** 180.
[13] H. Flaschka, *Mikrochim. Acta*, 1954, 361.
[14] P. Wehber, *ibid.*, 1955, 812.
[15] L. Erdey u. G. Rády, *Z. analyt. chem.*, 1956, **149,** 250.
[16] P. Wehber, *Mikrochim. Acta*, 1955, 927.
[17] *Idem, Z. analyt. Chem.*, 1956, **149,** 244.
[18] L. Erdey u. L. Pólos, *Analyt. Chim. Acta*, 1957, **17,** 458.
[19] L. Erdey, I. Buzás u. K. Vigh, *Talanta*, 1958, **1,** 377.
[20] L. Erdey, L. Mázor u. T. Meisel, *Mikrochim. Acta*, 1958, 140.
[21] L. Erdey u. L. Pólos, *Z. analyt. Chem.*, 1956, **153,** 411.
[22] L. Erdey u. F. Szabadváry, *Acta Chim. Hung.*, 1955, **6,** 131.
[23] *Idem, ibid.*, 1956 **8,** 191.
[24] *Idem, Z. analyt. Chem.*, 1957, **155,** 90.
[25] *Idem, Acta Chim. Hung.*, 1958, **13,** 335.
[26] *Idem, Z. analyt., Chem.*, 1958, **160,** 429.
[27] *Idem, Mikrochim. Acta* 1959, 424.
[28] L. Erdey, E. Zalay u. A. Bodor, *Acta Chim. Hung.*, 1957, **12,** 251.
[29] L. Erdey, E. Bányai, E. Zalay u. M. Tésy, *ibid.*, 1958, **15,** 65.
[30] L. F. Fieser u. H. T. Thompson, *J. Amer. Chem. Soc.*, 1939, **61,** 376.
[31] L. F. Fieser u. M. Fieser, *ibid.*, 1935, **57,** 491.
[32] R. L. Bent u. andere: *ibid.*, 1951, **73,** 3100.
[33] O. Ryba, J. Cifka, M. Malát u. V. Suk, *Coll. Czech. Chem. Comm.*, 1956, **21,** 349.
[34] A. Foffani u. U. Mazzucato, *Ricerca Scient.*, 1956, **26,** 2409.
[35] M. Březina u. P. Zuman, *Die Polarographie in der Medizin, Biochemie und Pharmazie*, Leipzig, 1956, S. 652.

[36] É. Bányai, L. Erdey u. F. Szabadváry, *Acta Chim. Hung.* (unter Druck).
[37] É. Bányai u. P. Zuman, *Coll. Czech. Chem. Comm.*, 1959, **24**, 522.
[38] L. Michaelis u. M. P. Schubert, *Chem. Revs.*, 1938, **19**, 437.
[39] L. F. Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 4915.
[40] W. M. Clark, B. Cohen u. H. D. Gibbs, *Hyg. Lab.*, 1928, **9**, 245.
[41] L. F. Oldfield u. J. O'M. Bockris, *J. Phys. Colloid Chem.*, 1951, **55**, 1255.

Talanta, 1959, Vol. 3, pp. 65 to 71. Pergamon Press Ltd. Printed in Northern Ireland

ORGANIC ANALYSIS—XV.* THE INFRARED SPECTRA OF THE TETRALIN SERIES

TSUTOMU MOMOSE, YO UEDA and HIROSHIGE YANO
Pharmaceutical Institute, Medical Faculty, University of Kyushu, Japan

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Summary—The out-of-plane CH deformation vibrations of the aromatic ring of the tetralin series normally appear in almost the same frequency region as in the corresponding benzene series, and their frequencies are regularly shifted by the type of substituents attached to the aromatic ring with a few exceptions.

All compounds which have an isolated CH group in the aromatic ring exhibit fairly strong absorption bands around the 800 cm^{-1} region, which may be associated with the aromatic ring.

Carbonyl and hydroxyl groups in the *peri*-position of tetralone are strongly chelated, showing frequency shifts in their stretching vibrations.

THE out-of-plane CH deformation vibrations of aromatic ring have been studied in detail in correlation to the position and type of substituents in the benzene,[1] pyridine,[2,3] naphthalene,[1,4,5] and quinoline[6] series, but no systematic study has appeared of the tetralin series in the literature. In this work, the infrared spectra of 61 compounds of tetralin series have been measured, and their out-of-plane CH deformation vibrations have been discussed. In the tetralone and 8-hydroxy-tetralin-7-acetic acid lactone derivatives, the C=O stretching vibrations were also discussed in relation to OH stretching vibrations.

RESULTS AND DISCUSSION

1. *Out-of-plane* CH *deformation vibrations*

The out-of-plane CH deformation vibrations of the aromatic ring of the tetralin series produced, generally, strong bands in almost the same region as the corresponding benzene series. Their frequencies showed regular shifts with the type of substituents present in the aromatic ring; and in general, strong electron-attracting substituents exerted shifts towards longer frequencies, and electron-donating substituents towards shorter frequencies. The substituents attached to the saturated ring gave no regular shift of the frequencies. These are shown in Table I and discussed in detail as follows.

1.1. *Four adjacent ring hydrogen atoms.* A few compounds thus substituted are shown in Table I, and exhibited strong absorption bands in the 740–770 cm^{-1} region. In agreement with Jones *et al.*,[7] who noted that the out-of-plane CH deformation vibrations of tetralin absorbed almost the same range of frequencies as *ortho*-disubstituted benzene derivatives, the above data coincided well with the 735–770 cm^{-1} region, which was proposed for *ortho*-disubstituted aromatics.[1]

1.2. *Three adjacent ring hydrogen atoms.* Compounds examined which had three adjacent hydrogen atoms were confined to derivatives of 8-tetralone and of the 8-hydroxy-7-acetic acid lactone. These compounds each had one strong band in the 785–815 cm^{-1} and 730–760 cm^{-1} regions, respectively, as shown in Table I. These

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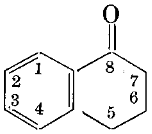
* Part XIV: *Chem. Pharm. Bull.* (*Tokyo*), in press.

bands correspond to those of the benzene series thus substituted, which appear in the 750–810 cm^{-1} and 680–725 cm^{-1} regions[1] or in the liquid state in the 780–830 cm^{-1} and 700–750 cm^{-1} regions.[8]

The two bands had variable intensities. The frequency of the higher component of the pair in the 8-tetralones varied with the substituent in the order $NO_2 > NHAc > OAc > OH$. This order agrees with the results obtained by Kross *et al.*[9] in mono-substituted and *para*-disubstituted benzene derivatives. Somewhat similar

Table I. Out-of-plane CH deformation frequencies

Tetralone-(8) derivatives



Substituent					Adjacent hydrogen atoms	δCH (cm^{-1})	
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(7)}$			
H	H	H	H	H	4	761*	
H	H	H	H	CO_2Et	4	771	
H	H	H	NO_2	H	3	815	759
NO_2	H	H	H	H	3	812	743
H	H	H	NHAc	H	3	808	735
H	H	H	OAc	H	3	807	737
H	H	H	OH	H	3	800	730
OH	H	H	H	CH_2CO_2H	2	824	
OMe	H	H	OMe	CH_2CO_2H	2	822	
OAc	H	H	OAc	H	2	842	
OH	H	H	OAc	H	2	842	
OH	H	H	OH	H	2	825	
OMe	H	H	OMe	H	2	812	
H	OH	H	H	CH_2CO_2H	2	833	
H	OMe	H	H	CH_2CO_2H	2	818	
H	NHAc	H	H	H	2	836	
H	NO_2	H	H	H	2	831	
H	OH	H	H	H	2	822	
H	H	OH	H	H	2	822	
H	OMe	H	H	H	2	821	
H	Me	H	H	H	2	815	

Tetralin derivatives

Substituent				Adjacent hydrogen atoms	δCH (cm^{-1})
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$		
H	H	H	H	4	744*
OAc	H	H	OAc	2	844
H	OH	H	H	2	822

8-Hydroxytetralin-7-acetic acid lactone derivatives

Substituent				Adjacent hydrogen atoms	δCH (cm^{-1})	
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$			
H	H	H	H	4	753	
H	H	H	NO_2	3	803	741
H	H	H	OAc	3	795	736
H	H	H	OH	3	787	746
OH	H	H	OH	2	821	
OAc	H	H	OAc	2	848	
H	OAc	H	H	2	833	

* Liquids; others in Nujol.

effects in the order of frequencies with substituent are apparent in the lower frequency component of the pair of bands in the 8-tetralones, and in the higher frequency component in the lactones.

1.3. *Two adjacent ring hydrogen atoms.* All compounds examined which had two adjacent hydrogen atoms in the 1:2, 2:3 or 3:4 positions absorbed strongly within the 810–850 cm^{-1} region. The frequency depended on the substituent, in the order OAc $>$ OH $\geqslant$ OMe, but the order $NO_2 >$ NHAc $>$ OAc $>$ OH remarked on above (in Section 1.2) was modified to NHAc $> NO_2$ in the tetralones with the two adjacent ring hydrogens.

2. *The* 800 cm^{-1} *absorption*

1:3-, 2:3-disubstituted, and 1:2:3-, and 1:2:4-trisubstituted compounds of the tetralin series which had an isolated CH group exhibited fairly strong absorption bands around the 800 cm^{-1} region as shown in Table II. These bands shifted towards longer frequencies with the nature of the substituents in the order OAc $>$ OH $>$ OMe in 2:3-disubstituted compounds, which coincides with the order obtained in their out-of-plane CH deformation vibrations. With the same substituents, the shift occurred toward longer frequencies in tetralin than it did in tetralone.

No satisfactory assignment was possible for the band, but the above nature of the shift might prove that the band was associated with the aromatic ring of the series. Some other compounds which had no isolated CH group sometimes showed absorption bands around the 800 cm^{-1} region, of variable intensity, but no agreement could be found with the position and number of the substituents.

3. C═O *and* OH *stretching vibrations*

The OH stretching frequencies of this series are shown in Table III. In the tetralone derivatives, the C═O stretching frequencies appeared in almost the same region as in aryl ketones, and are shown in Table IV.

3.1. *Hydroxy-tetralones.* The *peri*-hydroxyl group of the tetralone derivatives caused a large shift to shorter frequency, superimposing the absorption band on the absorption of Nujol. This fact proved that the group was strongly chelated with the carbonyl group. The other hydroxyl groups of tetralone gave no such shift.

TABLE II. THE 800 cm^{-1} ABSORPTION
2:3-Disubstituted derivatives

Compound	Substituent		Wave number (cm^{-1})
	$C_{(2)}$	$C_{(3)}$	
Tetralin	OMe	OMe	803
	OH	OH	809
	OAc	OAc	824
	OH	OMe	807
	OH	COMe	808
Tetralone-(8)	OMe	OMe	794
	OH	OH	805
	OAc	OAc	816
8-Tetralone-7-acetic acid	OMe	OMe	797
	OH	OH	806

1:3-, 1:2:3-, 1:2:4-Substituted tetralin derivatives

Substituent				Wave number (cm^{-1})
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	
OAc	H	OAc	H	823
OH	H	OH	H	812
NO_2	H	NO_2	H	799
NH_2	H	NH_2	H	817
OH	Me	H	OH	833
COMe	OH	OH	H	810
COMe	OMe	OMe	H	773
CHO	OH	OMe	H	776
$CH_2—CH=CH_2$	OH	OMe	H	811
C_3H_7	OH	OH	H	810
C_3H_7	OH	OMe	H	812
Me	OH	OMe	H	814
Br	OH	NO_2	H	798
Br	OMe	NO_2	H	798
Br	OMe	OMe	H	796

1:2:4-Substituted tetralone-(8) derivatives

Substituent				Wave number (cm^{-1})
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	
OMe	Me	H	OMe	813
OH	Me	H	OH	829

Measured in Nujol.

TABLE III. OH STRETCHING FREQUENCIES

Tetralone-(8) derivatives

Substituent					ν_{OH} (cm^{-1})	
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(7)}$		
OH	H	H	OAc	H		—
OH	H	H	OMe	H		—
OH	H	H	OH	H	3323	—
OH	H	H	OH	CH_2CO_2H	3554	—
OH	Me	H	OH	H	3280	—
H	OH	OH	H	H	3529	3206
H	OH	H	H	H		3237
H	H	H	OH	H		3209
H	OH	OH	H	CH_2CO_2H	3415	3253

Tetralin derivatives

Substituent				ν_{OH} (cm^{-1})	
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$		
H	OH	OH	H		3562
H	OH	OMe	H		3425
OH	H	OH	H	4072	3471

8-Hydroxytetralin-7-acetic acid lactone derivatives

Substituent				ν_{OH} (cm^{-1})	
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$		
OH	H	H	OH	3575	3287
H	H	H	OH		3361
H	OH	H	H		3405

Measured in Nujol.

Table IV shows that the C═O stretching vibrations of the *peri*-hydroxytetralone derivatives appear around 50 cm^{-1} lower in frequency than that of tetralone, showing that the vibrations are strongly influenced by hydrogen bonding. This shift is larger than the frequency shift of 40 cm^{-1} in *peri*-hydroxyanthraquinone,[10] and of 16–25 cm^{-1} in *peri*-hydroxynaphthoquinone. Other hydroxytetralones than the *peri*-hydroxy-derivatives also showed frequency shifts of about 35 cm^{-1} in C═O stretching vibrations, which might be caused by inter-molecular hydrogen bonding.

3.2. *γ-Lactones.* The C═O stretching vibrations of the γ-lactone in 8-hydroxytetralin-7-acetic acid lactones appeared in a frequency range of 1725–1790 cm^{-1}, and were fairly strongly affected by substituents attached to the aromatic ring. Table V

TABLE IV. C=O STRETCHING FREQUENCIES
Tetralone-(8) derivatives

Substituent					$\nu_{C=O}$ (cm^{-1})	$\Delta\nu_{C=O}$ (cm^{-1})
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(7)}$		
H	H	H	H	H	1684	0*
OH	H	H	OH	H	1612	−72
OH	H	H	OAc	H	1634	−50
OH	H	H	OMe	H	1637	−47
OAc	H	H	OAc	H	1695	+11
OMe	H	H	OMe	H	1679	−5
H	H	H	NO_2	H	1679	−5
NO_2	H	H	H	H	1693	+9
H	OH	H	H	H	1652	−32
H	OMe	H	H	H	1682	−2
H	Me	H	H	H	1679	−5
H	NO_2	H	H	H	1684	0
H	H	OH	H	H	1649	−35
H	OH	OH	H	H	1653	−31
H	OMe	OMe	H	H	1662	−22
H	OAc	OAc	H	H	1684	0
OMe	Me	H	OMe	H	1683	−1
OH	Me	H	OH	H	1618	−66
H	H	H	OH	H	1647	−37
H	H	H	OAc	H	1685	+1
H	OH	H	H	CH_2CO_2H	1663	−21
H	H	H	H	CO_2Et	1680	−4

* Liquid; others in Nujol.

TABLE V. C=O STRETCHING FREQUENCIES
8-Hydroxytetralin-7-acetic acid lactone derivatives

Substituent				$\nu_{C=O}$ (cm^{-1})	$\Delta\nu_{C=O}$ (cm^{-1})
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$		
H	H	H	H	1764	0
H	H	H	OH	1726	−38
OH	H	H	OH	1726	−38
H	OH	H	H	1742	−22
H	H	H	NO_2	1780	+16
H	NO_2	H	H	1789	+25
OAc	H	H	OAc	*ca.* 1770	*ca.* +6
H	H	H	OHc	*ca.* 1770	*ca.* +6
H	OAc	H	H	*ca.* 1770	*ca.* +6

Measured in Nujol.

shows their frequencies and shifts from the unsubstituted lactone. In the hydroxyl compounds, the shifts were 20–40 cm^{-1} towards lower frequencies, but were smaller in all cases where the hydroxyl group was acetylated, overlapping the absorption band of the C=O band of the acetyl group. This fact suggests that inter-molecular hydrogen bonding might be present in these compounds.* On the other hand, a nitro group attached to the aromatic ring exerted a shift towards the higher frequency region as may also be seen in the Table.

EXPERIMENTAL

Samples were previously[11] prepared in the writer's laboratory.

Infrared spectra were measured with Koken Model DS-201 and -301 recording infrared spectrophotometers using a NaCl prism.

Zusammenfassung—Die Infrarotspektren von 61 Verbindungen der Tetralinreihe wurden gemessen. Die Deformationsschwingungen der abstehenden CH-Gruppen wurdendiskutiert. Sie erscheinen im allgemeinen nahezu im gleichen Frequenzbereich wie die der entsprechenden Benzolreihe. Nur mit wenigen Ausnahmen werden ihre Frequenzen durch Substituenten regulär verschoben. Alle Verbindungen mit einer isolierten CH-Gruppe im aromatischen Ring zeigten eine ziemlich starke Absorptionsbande im 800 cm^{-1} Bereich. Carbonyl- oder Hydroxylgruppe in peri-Stellung im Tetralon sind stark cheliert und zeigen eine Frequenzverschiebung in den Streckschwingungen.

Résumé—Les spectres infra rouges de 61 composés des séries de la tétraline ont été déterminés et leurs vibrations "relatives" à la déformation des CH non plans ont été discutées. Celles-ci apparaissent, en général, à peu près dans le même domaine de fréquence que dans le cas des séries benzéniques correspondantes; à quelques exceptions près leurs fréquences varient régulièrement avec les substituants. Tous les composés comportant un groupement Ch isolé dans le cycle aromatique présentent, dans la région 800 cm^{-1}, des bandes d'absorption assez fortes qui peuvent être associées au cycle aromatique.

Le groupement carbonyl ou hydroxyl de la tétralone, placé en péri, est fortement chelaté et présente une variation de fréquence pour les vibrations de valence.

REFERENCES

[1] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules.* Methuen, London, 1958, p. 65.
[2] H. Shindo and N. Ikekawa, *Pharm. Bull.* (*Tokyo*), 1956, **4**, 192.
[3] H. Shindo, *ibid.*, 1957, **5**, 472.
[4] H. Kamata and Y. Nishino, *Bunseki Kagaku*, 1953, **2**, 338.
[5] H. Kamata and S. Tanaka, *ibid.*, 1956, **5**, 98.
[6] H. Shindo and S. Tamura, *Pharm. Bull.* (*Tokyo*), 1956, **4**, 292.
[7] R. N. Jones and C. Sandorfy, *Chemical Applications of Spectroscopy*, Interscience, New York, 1956, p. 391.
[8] T. Shimanouchi, *Kagaku-no-Ryoiki*, 1958, **12**, 314.
[9] R. D. Kross, V. A. Fassel and M. Margoshes, *J. Amer. Chem. Soc.*, 1956, **78**, 1332.
[10] M. St.C. Flett, *J. Chem. Soc.*, 1948, 1441.
[11] *cf.* T. Momose, H. Oya, Y. Ohkura and M. Iwasaki, *Pharm. Bull.* (*Tokyo*), 1954, **2**, 119; T. Momose, Y. Ohkura and S. Goya, *ibid.*, 1955, **3**, 401; T. Momose, T. Miki and K. Sawada, *ibid.*, 1955, **3**, 325; T. Momose and S. Goya, *Chem. Pharm. Bull.* (*Tokyo*), in press.

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* This assumption is supported by the fact that the C=O stretching frequency (1773 cm^{-1}) of γ-butyrolactone shifted to 1744 cm^{-1} when it was measured in phenol solution.

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UTILIZATION OF TERNARY AND ION-ASSOCIATION COMPLEXES IN CHEMICAL ANALYSIS—I

SELECTIVE EXTRACTION AND COLORIMETRIC DETERMINATION OF TRACES OF IRON AS "FERROÏN IODIDE"

FRANTIŠEK VYDRA and RUDOLF PŘIBIL
Laboratory of Analytical Chemistry, Chemical Institute, Czechoslovak
Academy of Sciences, Praha, Czechoslovakia

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Summary—The complex cation $Fe(Phen)_3^{2+}$ [Phen = 1:10-phenanthroline] reacts with certain anions forming slightly dissociated usually insoluble compounds, extractable by organic solvents, in particular chloroform and nitrobenzene, The iodide complex $Fe(Phen)_3I_2$ ("ferroïn iodide") has proved very suitable for the extraction and colorimetric determination of bivalent iron. High selectivity of the method is ensured by the addition of EDTA* which masks all the elements which require consideration in practice.

ONE of the most sensitive colorimetric determinations of traces of bivalent iron, using with 1:10-phenanthroline, is interfered with in many practical applications by the presence of certain cations. Phenanthroline is not a specific reagent for bivalent iron, and over a comparatively wide range of pH it reacts also with several other cations, forming soluble or insoluble, and usually also coloured complexes. Therefore the determination of iron is interfered with, for example, by the presence of silver, univalent and bivalent mercury (insoluble complexes) as well as by the presence of copper, cadmium, and cobalt (soluble, usually coloured complexes). Any colour of the test solution, whatever its cause, will interfere with the determination of iron because we must develop the colour reaction with phenanthroline directly in the solution. The phenanthroline complex with bivalent iron, $Fe(Phen)_3^{+2}$ is, however, not extractable by the usual organic solvents (in the presence of *e.g.* nitrates and sulphates). Therefore a way has been sought of improving this method. The extractability of the perchlorate complex of "ferroïn" by nitrobenzene makes possible, according to Margerun and Banks,[1] the determination of traces of iron in the presence of vanadium, chromium, manganese, nickel and zinc. The determination is interfered with according to these authors, by the presence of copper and cobalt which are also extracted as similar complexes into nitrobenzene. A short time ago Diehl and Buchanan[2] utilized the extraction of the phenanthroline-cyanide complex of bivalent iron $Fe(Phen)_2(CN)_2$ by chloroform or nitrobenzene for the colorimetric determination of iron in the presence of copper. The disadvantage of this method is that for each concentration of copper it is necessary to prepare a special calibration curve.

Many experiments have also been made to mask the interfering elements by complex-forming materials. An example is the determination of traces of iron in metallic bismuth suggested by Holmes[3] who uses ethylenediaminetetra-acetic acid for the screening of bismuth (adding it after the reduction of iron in acid medium before adding the phenanthroline).

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* EDTA = Ethylenediaminetetra-acetic acid.

The endeavour to improve the original colorimetric method of the determination of bivalent iron has also led many authors to study a wide range of derivatives of 1:10-phenanthroline. Smith and McCurdy,[4] for example, recommend for the colorimetric determination of copper and iron the as yet not readily available reagent 4:7-diphenyl-1:10-phenanthroline the complex of which, with copper and bivalent iron, is readily extractable by chloroform and nitrobenzene and has, in addition, a considerably higher extinction coefficient than "ferroïn" proper. According to the authors, cobalt, which is not extracted, should not interfere in this case. Because of the price of this reagent it cannot be expected that this method will have an extensive use in routine analysis.

In the course of a systematic study of the ternary complexes of phenanthroline of the type $Me(Phen)_3X_2$ (where $X = Cl, Br, I$ and CNS) we have also paid attention to the corresponding complexes of bivalent iron. Their comparatively slight solubility in water is already known from the paper by Blaue[5] who prepared many of them in solid form and analysed them. The iodide complex (subsequently called "ferroïn iodide") is very slightly soluble, and relatively undissociated. By preliminary experiments we have not only verified Blaue's results but have also confirmed our expectation that these ternary complexes are soluble in a number of organic solvents. The early experiments have proved that "ferroïn" can be quantitatively extracted by chloroform over a wide range of pH in the presence of iodide or sulphocyanide. Similar chloride and bromide complexes are not extracted. The increase of the selectivity of the "ferroïn iodide" extraction almost to the extent of absolute specificity was obtained with EDTA acid with which it is possible to screen practically all interfering bivalent to quadrivalent elements, under suitable conditions, without influencing the necessary reduction of tervalent iron to bivalent iron before the appropriate colorimetric determination.

EXPERIMENTAL

Reagents and solutions

Standard solutions of ferrous and ferric iron (0·05 molar) were prepared from reagent grade ferrous ammonium sulphate and ferric ammonium sulphate respectively. Their titres were determined gravimetrically. Solutions of $1 \cdot 10^{-3}$ and $1 \cdot 10^{-4}$ molar concentration were prepared by dilution.

Solutions of 1:10-phenanthroline ($5 \cdot 10^{-2}$ and $1 \cdot 10^{-3}$ molar) were prepared by dissolution of a precisely weighed and calculated quantity of 1:10-phenanthroline, Guaranteed Reagent (Lachema, National Corporation, Brno) in warm redistilled water acidified by a minimum quantity of nitric acid. The resulting pH of the solutions was 3 to 5.

Solutions of various metal salts were also prepared from reagent grade chemicals. The concentration of these solutions was controlled complexometrically.

The disodium salt of ethylenediaminetetra-acetic acid (EDTA) was used in solid form. The product "Chelaton 3" (Lachema, National Corporation, Brno) was employed.

30% solutions of potassium iodide and 20% solutions of potassium thiocyanate were also prepared from reagent grade chemicals.

Apparatus

The adjustment of the pH of the solutions was controlled potentiometrically with a glass electrode. The measurement was carried out with a pH meter, (Kovodružstvo, Praha).

The colorimetric measurement was carried out by a deflection photometer (Laboratorní potřeby, National Corporation, Praha) with the use of suitable filter.

The spectrophotometric measurements were carried out on a spectrophotometer (Uvispek, Hilger, London).

EXTRACTION OF BIVALENT IRON IN THE FORM OF ITS TERNARY COMPLEX WITH PHENANTHROLINE AND IODIDE

As mentioned in the introductory part it is possible to extract the red-orange complex of ferrous iron with 1:10-phenanthroline ("ferroïn") in the presence of excess of iodide ions by organic solvents, in particular by chloroform. In order to ascertain the basic optical properties of the chloroform solutions of various ternary complexes of bivalent iron the following series of tests was carried out:

A solution containing bivalent iron was mixed in a 100-ml beaker with phenanthroline solution, potassium iodide solution, and ammonium thiocyanate solution, diluted with water to approximately 25 ml and 25 ml of chloroform were added. The solution was thoroughly stirred by a magnetic stirrer. The chloroform layer was separated from water in a separating funnel with a long stem, then poured through a folded filter paper into a 25-ml measuring flask. The filter was rinsed with chloroform which was also collected into the flask. After adjustment to the mark the solution was measured photometrically in a 1-cm cell. If not otherwise mentioned the procedure was the same in all further measurements. The basic spectra are shown in the graphs of Fig. 1.

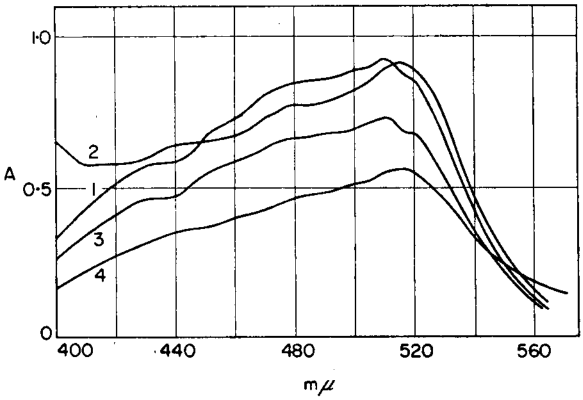

FIG. 1. Absorption spectra of complexes of ferrous iron ($4 \times 10^{-5}M$). (1) aqueous solution of "ferroïn," (2) chloroform solution of "ferroïn iodide", (3) aqueous solution of "ferroïn" thiocyanate (4) chloroform solution of "ferroïn thiocyanate."

Here curve (1) represents the absorption spectrum of "ferroïn" (the solution of "ferroïn iodide" in water has the same form) curve (2) represents the absorption spectrum of "ferroïn iodide" in chloroform, curve (3) the spectrum of "ferroïn thiocyanate" in water and finally curve (4) the spectrum of "ferroïn thiocyanate" in chloroform. All the measurements were made under the same conditions of concentration.

From the form of curves (1) and (2) it is evident that the extinction coefficient of "ferroïn" in water and of "ferroïn iodide" in chloroform is practically the same (in the range of maximum absorption); a change of the absorption occurs only in the region of shorter wave lengths and a slight shift of the absorption maximum, from 510 to 515 mμ, takes place. The absorption spectra of the aqueous and chloroform solutions of "ferroïn thiocyanate", however, differ from each other [curves (3) and (4)]. The shift of the absorption maximum is small but at the same time the decrease of the extinction coefficient is considerable. Because of the lower sensitivity the extinction of iron in the form of phenanthroline–thiocyanate complex has not been studied more closely.

DEPENDENCE OF THE EXTRACTION OF "FERROÏN IODIDE" ON THE CONCENTRATIONS OF 1:10-PHENANTHROLINE, IODIDE, ON pH AND ON THE TYPE OF THE ORGANIC SOLVENT USED.

Influence of the concentration of 1:10-*phenanthroline*

This has been followed by the method of the shift of balance (the so-called titration curve was measured). To a constant quantity of ferrous iron an increasing quantity of phenanthroline of the same molarity was added. The extraction was carried out with chloroform in the presence of a constant large excess of potassium iodide and by the same procedure as described in the preceding paragraph. Fig. 2 shows the curve obtained from the extinction values at 515 mμ.

From the form of the curve it is immediately evident that the extraction of "ferroïn iodide" (that is, the extinction of the extract) is constant above the ratio Fe^{+2} : Phen = 1 : 6. It is known that water solutions with excess of phenanthroline contain only complex with a ratio of components 1 : 3, *i.e.* with the composition $Fe(Phen)_3^{2+}$. The two breaks in the curve prove that the complex $Fe(Phen)_3I_2$ is extracted and, in the presence of excess of phenanthroline, also another complex containing also three further molecules of phenanthroline. (Note the sharp break on the curve in the proximity of the ratio 1 : 6). It is at present not possible without a more detailed study to decide how the further three molecules of phenanthroline are bonded. In nonaqueous (chloroform) medium a different behaviour of "ferroïn iodide" from that in water may be expected; but the presupposition that a solvate of the type $Fe(Phen)_3I_2.3$ Phen is being formed is hardly likely in view of the sharpness of the break in the proximity of the ratio 1 :6, which proves the comparatively considerable stability of the bonding of the further three molecules of phenanthroline in the extracted complex. A more detailed study of this question has not yet been carried out.

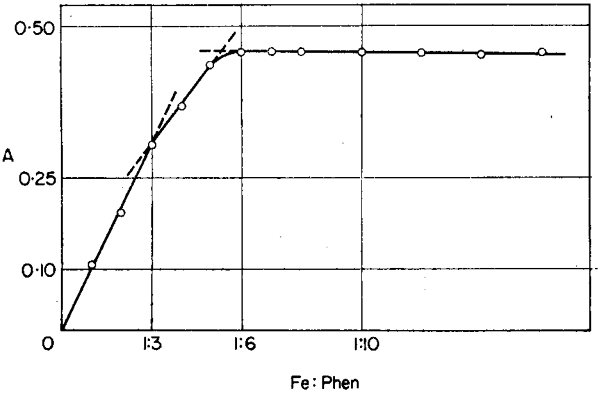

FIG. 2. Extinction of "ferroïn iodide" extract vs. excess of phenanthroline (titration curve). 25 ml of solution containing 1 ml of 1 × $10^{-3}M$ Fe^{2+}, 1 to 10 ml of 1 × $10^{-3}M$ 1:10-phenanthroline and 5 ml of 30% solution of KI extracted by 25 ml of chloroform.

Influence of KI *concentration*

A constant quantity of ferrous iron (4 · $10^{-5}M$) was extracted from solutions containing different amounts of potassium iodide in the presence of a constant quantity of phenanthroline and the light

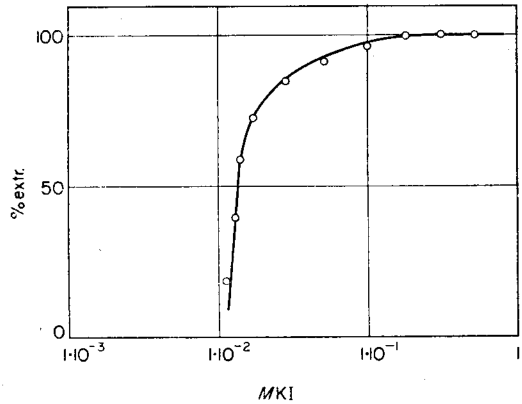

FIG. 3. Extraction (in %) of "ferroïn iodide" vs. concentration of iodide. Concentration of iron: 4 × $10^{-5}M$, of phenanthroline: 4 × $10^{-4}M$.

absorption of chloroform extracts was measured again. Fig. 3 shows the per cent extraction of bivalent iron as "ferroïn iodide" in relation to the molarity of the present potassium iodide. From the graph it is evident that only high concentrations of iodide (5000 times more than the iron) suppress the dissociation of small amounts of the complex $Fe(Phen)_3I_2$ so much that its quantitative formation as well as its quantitative extraction in chloroform is made possible. The removal of the complex from the water phase obviously influences this balance favourably.

Influence of pH

The completeness of the extraction in relation to the pH of the water solution was studied by preparing a water solution of "ferroïn iodide" under constant concentration conditions (the original pH being approximately 4), the pH of the solution being adjusted with 0·1*N* hydrochloric acid or 0·1*N* sodium hydroxide, controlling potentiometrically with a glass electrode to the required value; the solution was diluted to 25 ml and extracted by the already described method with 25 ml of chloroform. From the curve in Fig. 4 it is evident that the extraction is quantitative in the range pH 2·5–10 which in practice is the pH range of stability of "ferroïn".

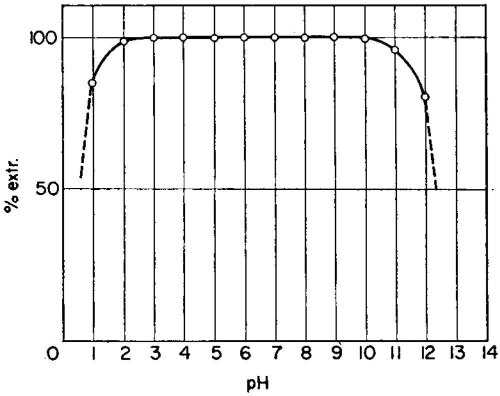

FIG. 4. Extraction (in %) of "ferroïn iodide" vs. pH. Concentration of iron: $4 \times 10^{-5}M$, of phenanthroline: $4 \times 10^{-4}M$ and of potassium iodide: $2 \times 10^{-1}M$.

Influence of the organic solvent

Besides chloroform, other solvents were also used for the extraction. The complex is only partly extracted by alcohols (aliphatic and aromatic). Ketones, hydrocarbons, tributylphosphate, carbon tetrachloride, carbon bisulphide or monochlorobenzene do not extract "ferroïn iodide" at all.

REDUCTION OF FERRIC IRON AND EXTRACTION OF "FERROÏN IODIDE" IN THE PRESENCE OF EDTA

It is known that the colorimetric determination of iron as "ferroïn" is interfered with by the presence of all elements forming sufficiently stable complexes with 1:10-phenanthroline. This is also the case in its determination as "ferroïn iodide" where, in addition, elements reacting with iodide, *e.g.* copper, lead etc., interfere. The interfering influence of all these elements can be totally eliminated by screening with EDTA. It was, of course, necessary to determine whether an excess of EDTA might not interfere in the extraction of bivalent iron. In normal analytical practice, however, iron is encountered in tervalent form. Therefore it was also necessary to study the conditions of the reduction of tervalent iron in the presence of high EDTA concentrations. That increase of selectivity in the colorimetric determination of iron is possible by using EDTA can be seen from Fig. 5, which shows the dependence on pH of the apparent stability constants[6,7,8] (conditions constant) of all four complexes $Fe(Phen)_3^{+2}$ (curve 2), $Fe(Phen)_3^{3+}$ (curve 3), FeY^{-2} (curve 4) and FeY^{-1} (curve 1). (Y = anion of EDTA). From curves (1) and (3) it is evident that the complex of tervalent iron with EDTA is much more stable than with phenanthroline. Curves (2) and (4), on the contrary, prove that, for example, at pH 5–6 the stability constant of "ferroïn" is approximately 15 times higher in order than the stability constant

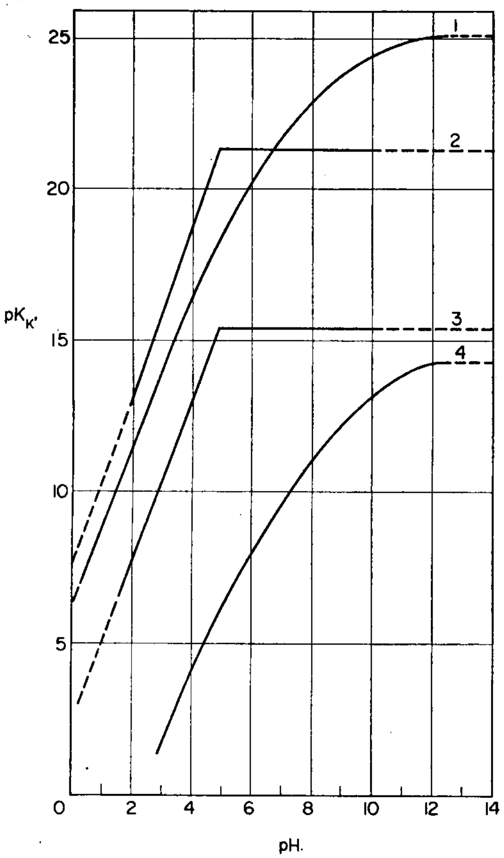

FIG. 5. Apparent stability constant vs. pH. (1) FeY^-; (2) $Fe(Phen)_3^{2+}$; (3) $Fe(Phen)_3^{3+}$; (4) FeY^{2-}

of the iron complex with EDTA. Therefore the formation of "ferroin" in the presence of EDTA must follow a completely smooth course at the given pH assuming that the tervalent iron compounded in a complex with EDTA is quantitatively reduced. A series of tests was therefore carried out on the reduction of the complex FeY^{-1} in the presence of phenanthroline which, according to the equation (1), should in fact encourage the reduction of tervalent iron:

$$FeY^- + 3\,\text{Phen} + e^{-1} + 2H^{+1} \rightleftharpoons Fe(\text{Phen})_3^{+2} + H_2Y^{-2} \qquad (1)$$

Hydroxylamine has proved satisfactory for the reduction of iron, especially at increased temperature (approximately 50°). Tests have confirmed our theoretical assumption that the reduction of tervalent iron is quantitative in the presence of practically any amount of EDTA if a sufficient quantity of phenanthroline is simultaneously present and the pH of the solution is suitable (influence of pH on the redox potential of the system). In solutions of pH 5–8 at a temperature of approximately 50° the reduction of iron is smooth and quantitative in the presence of about twenty times as much phenanthroline as iron. A sufficient excess of hydroxylamine is used for the reduction. The extraction of the already formed "ferroïn iodide" is also not interfered with by the presence of EDTA. Proof of this is found in Fig. 6. The points on the calibration curve marked with a circle indicate the extinction values for the "ferroïn iodide" extract, and those marked with a square show the extinction of "ferroïn iodide" in the presence of 1 g of EDTA in 25 ml of aqueous phase.

The calibration curve was obtained by the following series of tests: a solution containing ferric ammonium sulphate (0·44–3·79 μg in 1 ml) was diluted to about 10 ml, the pH value was adjusted with aqueous ammonia (1 : 1) to pH 7–8 (glass electrode). After addition of 5 ml of 10% solution of hydroxylamine hydrochloride (previously neutralized to pH 7–8) and of 4 ml of 0·05 molar phenanthroline

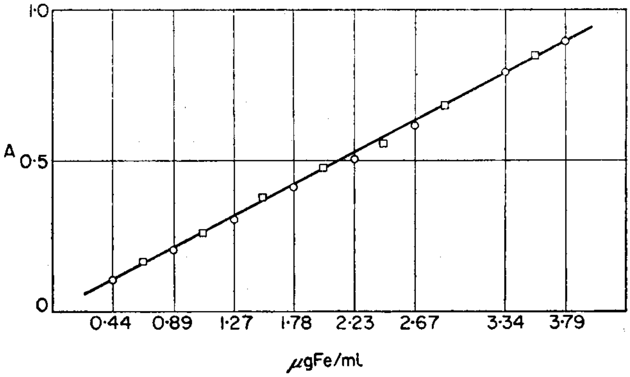

FIG. 6. Calibration curve for the determination of iron as "ferroïn iodide" ○ for "ferroïn iodide" ⊡ for "ferroïn iodide" in the presence of EDTA.

the solution was heated to 40° to 60°. After 2 minutes the solution was cooled to room temperature, 5 ml of 30% solution of potassium iodide were added, the solution was diluted to 25 ml and extracted with 25 ml of chloroform as described above. The light absorption was measured on a colorimeter with the use of a 510 mμ filter. A series of tests with solutions containing 1 g of EDTA (EDTA is dissolved only after adjusting the pH of the solution) was carried out in the same manner.

TABLE I. DETERMINATION OF IRON BY EXTRACTION OF "FERROÏN IODIDE" WITH CHLOROFORM IN THE PRESENCE OF A NUMBER OF METALS*

Present		Found	
Fe μg/ml	Other metal mg/ml	Fe μg/ml	Error in %
0·66	—	0·68	+3·3
1·32	—	1·31	−0·7
1·98	—	1·95	−1·5
2·64	—	2·64	0·0
3·33	—	3·30	−1·0
3·96	—	3·91	−1·2
2·64	2·3 Ni	2·66	+0·8
2·64	2·7 Zn	2·64	0·0
2.64	3·1 Mn	2·67	+1·2
2·64	2·0 Cr	2·68	+1·4
2·64	29·0 Bi	2·64	0·0
2·64	28·0 Pb	2·66	+0·8
2·64	2·7 Al	2·62	−0·8
2·64	21·0 U	2·64	0·0
2·64	1·9 Ti	2·67	+1·2
2·64	9·1 Zr	2·62	−0·8
2·64	26·0 Th	2·61	−1·2
2·64	11·0 Cd	2·68	+1·2
2·64	8·0 Cu	2·64	0·0
2·64	4·6 Co	2·68	+1·4

* The stated results are the mean value of three determinations.

DETERMINATION OF TRACES OF IRON IN THE PRESENCE OF OTHER ELEMENTS

By the method just described it is possible to determine traces of iron in the presence of a range of elements if they are screened by EDTA; this also prevents hydrolysis of certain elements which would otherwise not interfere in the determination. Both the masking and the extraction can be carried out in the pH range 5–8. Copper and cobalt are an exception. Copper can be completely masked against phenanthroline by means of EDTA at pH 7–8 (it is possible also at higher pH but here the sensitivity of the reaction of phenanthroline with ferrous iron decreases). Small quantities of cobalt are screened by EDTA at pH values above 9. Higher concentrations, however, interfere at this pH since the phenanthroline-iodide complex of cobalt is formed and this is also extractable. A subsequent paper will discuss the selective extraction and analytical utilization of this complex. In the presence of cobalt it is therefore necessary to modify the procedure by previously converting the cobalt into the complex of tervalent cobalt with EDTA. In the presence of copper it is sufficient to adjust the pH of the solution to a value of 7–8 before the reduction with hydroxylamine.

TABLE II. DETERMINATION OF IRON IN METALS AND ALLOYS

Sample	Composition, %	Content of Fe, %	Found, Fe,* %
Pure "cobalte"	99·40 Co, 0·42 Ni 0·03 Cu, 0·04 Cr 0·22 Si, traces of P, S, As	0·10	0·096
Bronze	58·4 Cu, 39·20 Zn 1·02 Pb, 0·12 Ni 0·33 Al, 0·01 Mn 0·02 Si, 0·48 Sn 0·02 Mg, 0·01 Ag	0·40	0·403
Waspaloy NBS, No. 349	57·14 Ni, 19·45 Cr 13·95 Co, 4·03 Mo 3·11 Ti, 1·25 Al 0·30 Si, 0·42 Mn 0·006 Cu, 0·077 Zr 0·0043 B, 0·074 C traces of P and S	0·142	0·138

* The stated results of the determination of iron are the mean value of three determinations.

DETERMINATION OF TRACES OF IRON IN THE PRESENCE OF COBALT

Procedure: To 5 ml of the solution (2 to 20 µg per 1 ml) add an amount of EDTA sufficient to bond cobalt (and other elements), adjust the pH to 7–8 and add several drops of 10% hydrogen peroxide. Oxidize the cobalt to the tervalent form (CoY^{-1}) and simultaneously remove the excess of peroxide by boiling for several minutes. After cooling to approximately 50° add 5 ml of 10% hydroxylamine hydrochloride solution (pH 7–8) and 4 ml of 0·05 molar phenanthroline. After cooling proceed as already mentioned. Table I shows typical results for the determination of traces of iron in the presence of various elements.

PRACTICAL APPLICATION

The suggested method has proved satisfactory in certain samples—"pure cobalt", bronze and a special alloy. After dissolution of the sample in nitric acid or in *aqua regia* the solution was adjusted to a suitable volume. In an aliquot (usually 5 ml) iron was determined by the method described. Oxidation with hydrogen peroxide was carried out in samples containing cobalt. The results are given in Table II.

Acknowledgement—The authors wish to thank Dr. K. L. Cheng, Metals Division, Kelsey-Hayes Comp., Utica, N.Y. for supplying a sample of the alloy Waspaloy used in this work.

Zusammenfassung—Das komplexe Kation $Fe(Phen)_3^{2+}$ (Phen = 1,10-Phenantrolin) reagiert mit gewissen Anionen unter Bildung schwach dissoziierter oder praktisch unlöslicher Verbindungen, die mit organischen Lösemitteln (vorwiegend Chloroform und Nitrobenzol) ausgeschüttelt werden können. Der Komplex $Fe(Phen)_3J_2$ ("Ferroinjodid") hat sich fur die Extraktion und photometrische Bestimmung von zweiwertigem Eisen als äusserst brauchbar erwiesen. Hohe Selektivität der Methode wird durch Zugabe von ÄDTA erreicht, wodurch alle üblichen Störmetalle ausgeschaltet werden.

Résumé—Le cation complexe $Fe(Phen)_3^{2+}$ (où Phen = 1:10 phenanthroline) réagit avec certains anions en donnant des composés peu dissociés et pratiquement insolubles, extractibles par des solvants organiques principalement par le chloroforme et le nitrobenzène. Le complexe iodure $Fe(Phen)_3I_2$ (iodure de ferrïone) s'est révélé tres adapté pour l'extraction et le dosage colorimétrique du fer divalent. La grande sélectivité de la méthode est augmentée par l'addition de EDTA qui élimine tous les éléments dont on doit tenir compte en pratique.

REFERENCES

[1] B. W. Margerum and C. V. Banks, *Analyt. Chem.*, 1954, **26**, 200.
[2] H. Diehl and E. B. Buchanan, *Talanta* 1958, **1**, 76.
[3] D. G. Holmes, *Analyst*, 1957, **82**, 528.
[4] G. F. Smith and W. H. McCurdy Jr., *Analyt. Chem.*, 1952, **24**, 371.
[5] F. Blau, *Mh. Chem.*, 1898, **19**, 647.
[6] A. Ringbom and E. Wänninen, *Analyt. Chim. Acta*, 1954, **11**, 153.
[7] G. Charlot and R. Gauguin, *Les méthodes d'analyse des reactions en solution*, Masson, Paris, 1951, p. 177.
[8] R. Přibil and F. Vydra, In press.

Talanta, 1959, Vol. 3, pp. 81 to 90. Pergamon Press Ltd. Printed in Northern Ireland

ANALYTICAL APPLICATIONS OF XYLENOL ORANGE—III. SPECTROPHOTOMETRIC STUDY ON THE HAFNIUM-XYLENOL ORANGE COMPLEX

K. L. CHENG
Metals Division, Kelsey-Hayes Co., New Hartford, N.Y., U.S.A.

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Summary—Hafnium reacts similarly to zirconium with Xylenol Orange. The hafnium–Xylenol Orange complex shows almost identical maximum absorption as the zirconium–Xylenol Orange complex at 535–540 mμ. The reagent gives a more sensitive reaction with hafnium than with zirconium. The molar absorption of the hafnium–Xylenol Orange complex was found to be 48,700 at 540 mμ. The formation constant of the hafnium complex was calculated as 3.2×10^6 in $0.3N$ perchloric acid. The conditions for using Xylenol Orange as a reagent for determining hafnium have been studied. Only zirconium or hafnium gives a purplish-red colour reaction with Xylenol Orange in $0.8N$ perchloric acid in the presence of hydroxylamine hydrochloride, which masks both iron and bismuth. Hafnium may be distinguished from zirconium since zirconium can be masked by hydrogen peroxide. Beryllium may be used as a demasking agent in the determination of zirconium or hafnium in the presence of fluoride.

INTRODUCTION

IN previous papers,[1,2] Xylenol Orange has been successfully used as a sensitive and selective reagent for zirconium. The zirconium-Xylenol Orange complex has been investigated spectrophotometically.[3] Recently this laboratory needed a sensitive method for determining small amounts of hafnium in high temperature alloys. This paper describes the results of a spectrophotometric study on the hafnium-Xylenol Orange complex and the application of this reagent to the determination of trace amounts of hafnium.

EXPERIMENTAL

Reagents

Xylenol Orange solution: 0.05% aqueous solution. This gave a concentration of $8 \times 10^{-4}M$. A $4 \times 10^{-5}M$ solution in $0.8N$ perchloric acid was prepared by appropriate dilution.

Standard hafnium solution: Accurately weighed, 0.1786 g of super-pure hafnium, prepared by the iodide process, was carefully dissolved in a platinum crucible by adding 1 ml of concentrated hydrochloric acid, 5 ml of water, and 2 to 3 drops of hydrofluoric acid. It was covered and gently warmed until all hafnium was in solution. The cover was rinsed with the minimum amount of water into the crucible. The content was evaporated to a few ml on a hot plate which was covered with asbestos. It was evaporated again, after addition of 4 ml of concentrated sulphuric acid, until it was fumed to a volume of approximately 1 to 2 ml. After cooling, 10 ml of water were carefully added, upon which hafnium was precipitated. The crucible was covered and heated until the precipitate was dissolved. After cooling, it was transferred into a 100-ml volumetric flask, rinsed, and made up to volume with $0.3N$ perchloric acid. This solution was presumably to be $0.0100M$. It was found to be 0.0099_4M by EDTA standardization. A solution containing 5 to 10 μg hafnium per ml was prepared by appropriate dilution.

EDTA standardization of hafnium solution: Attempted standardization of the hafnium solution by direct EDTA titration at pH 1 using Xylenol Orange as the indicator gave no sharp end-point whether the titration was carried out at room temperature or at 100°. Addition of a slight excess EDTA and back-titration with a standard copper nitrate solution at pH 3 to 5 using PAN as the indicator gave a gradually fading end-point as copper displaced hafnium. A good end-point with PAN at pH 6 was obtained by using a zinc solution as the back titrant. To 10 ml of approximately $0.01M$ hafnium solution in a porcelain dish or crucible were added 25 ml of $0.005M$ standard EDTA solution. After adjusting the pH to approximately 6 to 7, the solution was back-titrated with a standard $0.005M$ zinc solution using 4 drops of 0.1% PAN solution as the indicator. The end-point change was from yellow to faint pink. In the previous work zirconium was successfully standardized either by the direct EDTA titration at pH 1 using Xylenol Orange as the indicator at 80° or by the EDTA back-titration, with copper as the back titrant, at pH 3 using PAN as the indicator. The stability constants (log K) of the EDTA complexes of zirconium, hafnium, and copper have been reported to be 19.9, 19.2, and 18.8 respectively. From the reported values, it is interesting to note that hafnium behaved differently from zirconium in the EDTA titration under similar conditions.

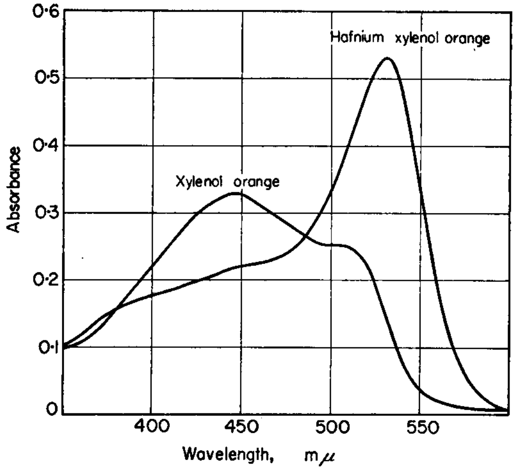


FIG. 1.—Spectra of Xylenol Orange and its hafnium complex.

The absorbance measurements were made with a Cary Spectrophotometer, Model 14, and a Beckman Spectrophotometer, Model DU. A Dyna Cath was used for the mercury cathode separation.

Spectra

Fig. 1 shows that the maximum absorption of the hafnium–Xylenol Orange complex is at 530 mμ in $0.3N$ perchloric acid. A wavelength of 535 mμ is suggested for the measurement since it offers maximum absorption when Xylenol Orange is used as the blank. This wavelength is almost identical with the maximum absorption wavelength of the zirconium–Xylenol Orange complex. It is also noted that in $0.8N$ perchloric acid medium the pure Xylenol Orange solution showed a small peak at 507 mμ and that the zirconium Xylenol Orange complex had a small peak at 340 mμ.

Calibration curve

To 25-ml volumetric flasks were added 0, 1, 2, 4, 6, 8, and 9 ml of $5 \times 10^{-5}M$ hafnium solution and 3 ml of $8 \times 10^{-4}M$ Xylenol Orange solution in $0.3N$ perchloric acid. The flasks were made to volume with $0.3N$ perchloric acid. The absorbance measurements were made at 540 mμ using a reagent blank. Beer's law was followed. For more than 80 μg hafnium in 25 ml the absorbance was slightly off the straight line. By increasing the amount of Xylenol Orange, Beer's law may follow for larger amounts of hafnium. Since the colour develops rapidly and is stable, no particular attention need be paid to the time of standing. Fig. 2 shows calibration curves with and without addition of hydrogen peroxide. Since hydrogen peroxide also diminishes the colour intensity of the hafnium complex, it would therefore be expected that the curve with addition of hydrogen peroxide would be different from that without hydrogen peroxide.

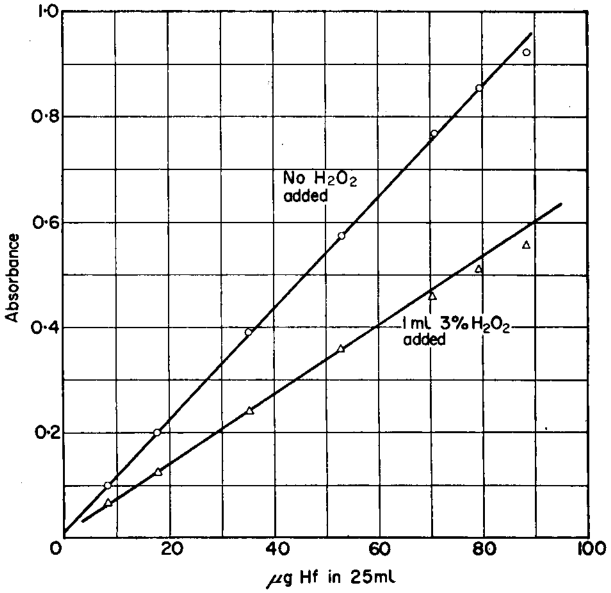


FIG. 2.—Calibration curve.

Specificity

In Part I of this series, the qualitative results of Xylenol Orange in 0.2*N* sulphuric acid medium indicate that niobium, tin,^{II} and molybdenum also gave light pink or yellow-orange colours as well as hafnium, zirconium, iron^{III}, and bismuth. It was also true that in 0.3*N* perchloric acid, in the presence of hydroxylamine hydrochloride and 0.8*N* perchloric acid, only zirconium and hafnium gave a purplish-red colour. Such a colour reaction seems to be highly selective for zirconium or hafnium under the conditions tested. Hydrogen peroxide formed a precipitate or complex with zirconium in 0.5*N* to 1.0*N* perchloric acid medium and had less effect on hafnium under similar conditions. Therefore, it was possible to distinguish the two metals. A simple test was conducted: One drop of 0.01*M* zirconium or hafnium solution (in 0.2*N* sulphuric acid) was mixed with 4 to 5 drops of 0.8*N* perchloric acid and one drop of 30% hydrogen peroxide. Zirconium did not give any significant colour change and hafnium gave a red to purplish colour upon addition of one drop of 0.05% Xylenol Orange solution.

Sensitivity

The Xylenol Orange in 0.8*N* perchloric acid gave a less sensitive colour reaction with hafnium than with zirconium. The molar absorption of the hafnium-Xylenol Orange complex was found to be 25,100 at 535 mμ as compared with 38,800 for that of the zirconium-Xylenol Orange complex at 540 mμ in 0.8*N* perchloric acid medium. However, in the optimum acid concentration of 0.3*N* perchloric acid, the molar absorption of the hafnium complex was found to be 48,700, which is much higher than that of the zirconium complex.[3]

Effect of anions

Anions such as EDTA, oxalate, phosphate, thiosulphate, fluoride, and sulphate inhibited the colour of the hafnium complex as well as that of the zirconium complex. As compared with the zirconium complex, the hafnium complex could tolerate less sulphate (see Fig. 3). Large amounts of thioglycollic acid also decreased the absorbance slightly. If 1 ml of 1% thioglycollic acid is used, the same amount of thioglycollic acid should be added in preparing the calibration curve. The interference of fluoride could be eliminated by beryllium. The results of determining zirconium or hafnium in the presence of fluoride are shown in Table I. For amounts of fluoride and zirconium or hafnium studied, the optimum amount of beryllium required is 1.5 millimoles. Apparently fluoride formed a

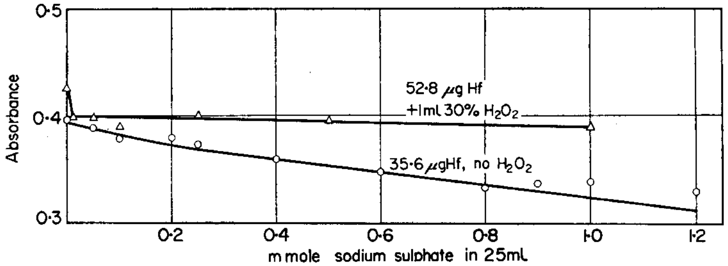


FIG. 3.—Effect of sulphate

TABLE I. DETERMINATION OF ZIRCONIUM AND HAFNIUM IN PRESENCE OF FLUORIDE BY USING BERYLLIUM AS DEMASKING AGENT

Zirconium

Metal present, *millimole* × 10^{-4}	Potassium fluoride added, *millimole* × 10^{-4}	Beryllium chloride added, *millimole* × 10^{-4}	Recovery, %
1.92	10	10	58.2
1.92	10	100	52.8
1.92	10	1,000	72.0
1.92	10	1,500	72.7
1.92	10	10,000	97.7
1.92	10	15,000	100.5
1.92	10	20,000	107.5
none	none	20,000	0.0

Hafnium

Metal present, *millimole* × 10^{-4}	Potassium fluoride added, *millimole* × 10^{-4}	Beryllium chloride added, *millimole* × 10^{-4}	Recovery, %
1.92	10	10	91.1
1.92	10	100	92.4
1.92	10	1,000	101.6
1.92	10	10,000	105.0
1.92	10	20,000	108.0
3.84	10	1,000	98.5
3.84	20	1,000	89.9
3.84	20	1,500	93.0
3.84	20	10,000	96.5
3.84	20	15,000	105.3
3.84	20	20,000	109.5
none	none	20,000	1.8

stronger complex with zirconium in $0.8N$ perchloric acid than with hafnium in $0.3N$ perchloric acid, and therefore more beryllium was needed to demask fluoride which masked the zirconium colour. Since large amounts of beryllium salt gave a slight blank in the $0.3N$ perchloric acid medium, a blank determination should be made. It was also noticed that large amounts of chloride gave slightly higher absorbance. Aluminium could also be used for demasking fluoride but proved less efficient than beryllium. Under the experimental conditions boric acid could not demask fluoride from the zirconium or hafnium complex.

Effect of acid concentration

The effect of acid concentrations on the colour development of the Xylenol Orange complexes of zirconium was different from that for hafnium, (see Fig. 4 and compare Fig. 3 in reference[1].) The optimum acid concentration for the hafnium complex was 0.3*N* of perchloric acid. Acid concentrations higher than 0.4*N* greatly diminished the colour intensity. The hafnium complex tolerated less, and required a narrower range of acid concentration. The acidity should be carefully controlled, since increase in acidity tended to shift the maximum absorption of the Xylenol Orange solution to a longer wavelength.

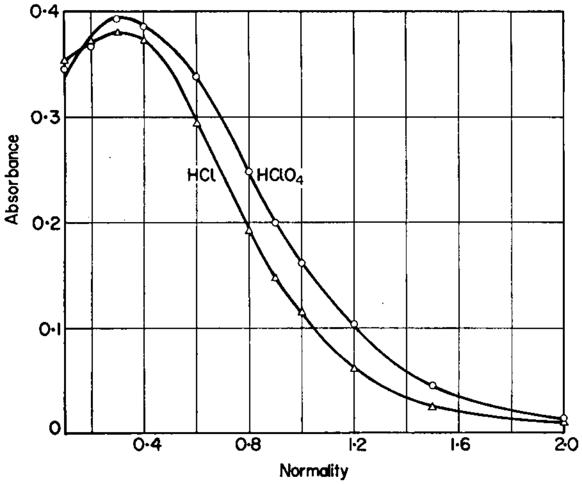


FIG. 4.—Effect of acid concentration.

An attempt was made to determine hafnium in the presence of zirconium through control of acidity. Both the hafnium and zirconium complexes absorb appreciably in 0.5*N* perchloric acid, while in 1.0*N* perchloric acid only the zirconium complex absorbs appreciably. Thus if the colour of a mixture of zirconium and hafnium solution is developed at 0.6*N* acidity and later at 1.0*N* acidity, the difference of the absorbance would represent the amount of hafnium. The actual results obtained were about 20–30% high, probably due to difficulty in control of acidity.

Effect of Xylenol Orange

In 0.3*N* perchloric acid, 3 ml of 0.05% Xylenol Orange are recommended for from 10 to 80 μg of hafnium. Too large amounts of the dye tended to decrease the absorbance. It is possible that in the presence of large excess of the dye, zirconium or hafnium may form a complex other than a 1 : 1 complex. The dye may be expected to vary in purity from lot to lot, and therefore a new calibration curve should be prepared for each fresh lot of dye used.

Formation constant

The mole ratio and the formation constant of the hafnium–Xylenol Orange complex has been determined spectrophotometrically by the same method as that previously reported for the zirconium–Xylenol Orange complex. It is evident that hafnium like zirconium also formed a 1 : 1 complex with Xylenol Orange. The formation constant (K_f) for the hafnium–Xylenol Orange complex in 0.3*N* perchloric acid was calculated from Job's curves, shown in Fig. 5, as 3.2×10^6. It is slightly lower than that of the zirconium–Xylenol Orange complex[8] ($K_f = 4.0 \times 10^7$). It seems to agree with the general trend that hafnium forms a slightly less stable complex than zirconium.

Masking effect of hydrogen peroxide

It was reported previously from qualitative tests that hydrogen peroxide could easily mask the zirconium–Xylenol Orange complex in 0.2*N* sulphuric acid medium, but not the hafnium–Xylenol Orange complex. An extensive investigation was made to see if this masking action could be utilized in the determination of hafnium in the presence of zirconium.

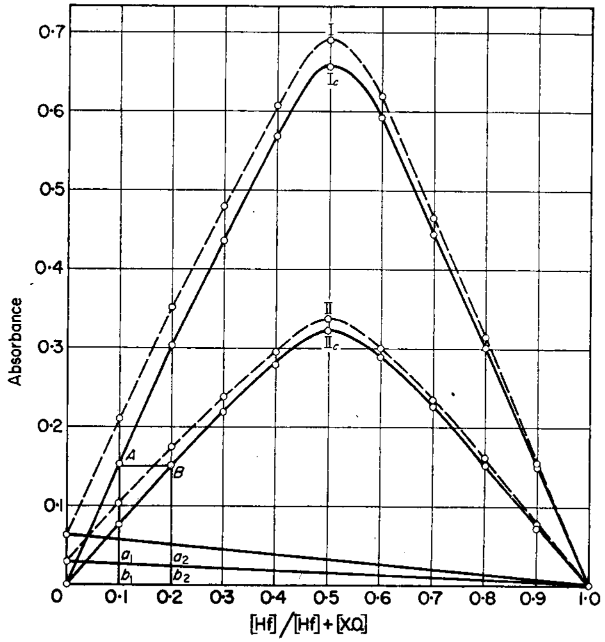


FIG. 5.—Job's curves.
I_c and II_c are corrected curves of I and II respectively.

Effect of hydrogen peroxide on absorbance of pure hafnium solutions: Addition of from 1–4 ml of 15% hydrogen peroxide per 25 ml, before addition of Xylenol Orange to a hafnium solution gave a lower absorbance than that with no hydrogen peroxide added. The absorbance increased gradually with time of standing, reaching a maximum value between 1.5 and 2.0 hours (Fig. 6). Heating hastened the colour development but the colour faded rapidly. A calibration curve prepared from 10 to 80 μg hafnium with 2 ml 15% hydrogen peroxide and 1.5 to 2.0 hours standing also followed Beer's law. But the slope of the curve was lower than that prepared without hydrogen peroxide. When hydrogen peroxide was added after the colour had been developed, the colour decreased with time and merged after about 3 hours with the curve prepared by addition of hydrogen peroxide before the colour had been developed. During the first 10 to 15 minutes, however, the absorbance was essentially constant, thus offering a possibility of measuring the absorbance, which was only slightly lower than that without hydrogen peroxide at its maximum. A calibration curve prepared under this condition also followed Beer's law. Hydrogen peroxide inhibited almost completely the colour development of the zirconium–Xylenol Orange complex regardless of whether the hydrogen peroxide was added before or after the colour development. The absorbance varied only slightly with lapse of time.

Effect of hydrogen peroxide on recovery of hafnium in the presence of zirconium: From the results shown in Fig. 6, it can readily be assumed that the determination of hafnium in the presence of zirconium, or *vice versa*, would be possible. However, the experimental results were not so satisfactory as expected. Table II indicates that the presence of 17.5 μg of zirconium does not show any significant effect on the absorbance of the hafnium–Xylenol Orange complex, but that larger amounts of zirconium decrease the absorbance of the hafnium complex. Various mixtures of hafnium and

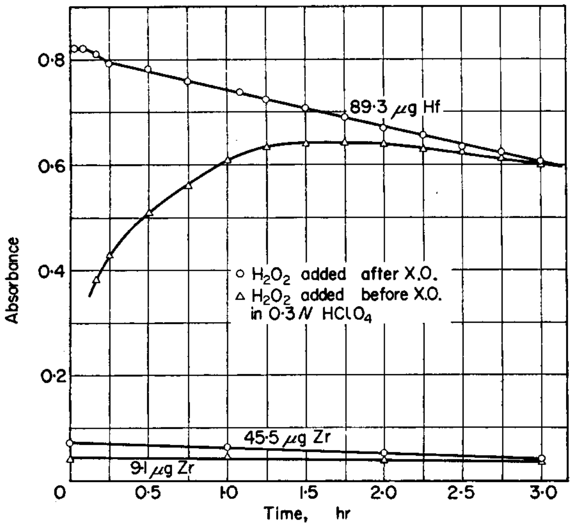
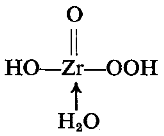


FIG. 6.—Effect of standing.

zirconium were analyzed for hafnium recovery. The results in Table II show that the smallest amount of hafnium (17.5 μg) gave the best recoveries with both curves. By using the curve with 52.5 μg of zirconium added, the average recovery of known amounts of hafnium was approximately ±5%. The present results suggest a new approach to the study of the selective determination of zirconium in the presence of hafnium and *vice versa* through the use of other complexing agents in a manner analogous to the use of Xylenol Orange and hydrogen peroxide.

The masking action of hydrogen peroxide on the zirconium Xylenol Orange complex is probably based on the formation of a relatively stable zirconyl peroxide complex:



$$\begin{array}{c} \text{O} \\ \| \\ \text{HO—Zr—OOH} \\ \uparrow \\ \text{H}_2\text{O} \end{array}$$

Though the formation constant of zirconyl peroxide is not known, it is presumably not greatly different from that of the zirconium–Xylenol Orange complex because the change in concentration of hydrogen peroxide or Xylenol Orange would shift the following equilibrium,

$$\text{Zr-Xylenol Orange} + H_2O_2 \rightleftharpoons \text{zirconyl peroxide} + \text{Xylenol Orange.}$$

It is rather difficult to understand the fact that the presence of relatively large amounts of zirconium tended to decrease the recovery of hafnium. Further study is needed to ascertain if the masking action of hydrogen peroxide can be applied to the quantitative determination of hafnium in the presence of wide range of zirconium. However, from the present results, it may be applied to the estimation of purity of hafnium metal or its salt when pure hafnium metal is available as a standard.

Effect of sulphate in presence of hydrogen peroxide: When hydrogen peroxide is present, 0.01 to 10 mmole of sulphate gave a constant absorbance for the hafnium–Xylenol Orange complex (Fig. 3). This is different behaviour from that caused by the addition of sulphate to the sample in the absence of peroxide, where the absorbance decreased rapidly. Addition of 0.1 mmole of sulphate gave slightly higher absorbance of the hafnium–Xylenol Orange complex in the presence of peroxide than in the absence of peroxide.

Effect of other compounds in presence of hydrogen peroxide: For the solution containing 68.6 μg hafnium, 35.0 μg zirconium and 1 ml of 30% hydrogen peroxide, approximately 75% to 77%

TABLE II. DETERMINATION OF HAFNIUM IN HAFNIUM AND ZIRCONIUM MIXTURE USING HYDROGEN PEROXIDE AS MASKING AGENT

Mixture, μg		Hafnium found			
		Reference: 17.5 μg Zr		Reference: 52.5 μg Zr	
Hf	Zr	μg	% Recovery	μg	% Recovery
17.15	17.5	18.5	107.0	17.15	100.0
17.15	35.0	19.5	112.5	16.0	96.2
17.15	52.5	18.0	104.2	17.3	101.5
17.15	105.0	16.7	96.5	15.8	94.0
34.3	17.5	39.5	116.0	41.0	117.0
34.3	35.0	38.5	113.2	38.1	110.0
34.3	52.5	34.6	101.4	36.3	105.0
34.3	105.0	28.8	84.7	26.8	80.9
68.6	17.5	73.2	106.4	92.0	131.7
68.6	35.0	67.8	98.6	73.5	105.7
68.6	52.5	62.5	91.0	76.0	108.7
68.6	105.0	50.7	73.3	4815	71.5

recoveries were obtained by addition of 1 ml of 1% gelatine, glycerine, polyvinyl alcohol, sucrose, mannitol, resorcinol, pyrocatechol, pyragallol, *tris*(hydroxymethyl)-aminomethane, acetic acid, or formic acid. By adding 1 ml of 1% ethyleneglycol-bis-(β-aminoethylether) N:N′-tetra-acetic acid or oxalic acid, a recovery of 66.5% or 3.6% was obtained. By addition of 2 to 3 ml of 1% lactic acid, a recovery of 93.5% was obtained.

DETERMINATION OF THE HAFNIUM IN HIGH-TEMPERATURE ALLOY

The determination of hafnium in the presence of zirconium cannot be relied upon at the present time. In the absence of zirconium, however, a method to determine hafnium in the concentration range of 0.01–0.5% has been developed for Udimet 500, a nickel-base alloy containing about 3% Al, 3% Ti, 3–5% Mo, 18–20% Cr, 16–20% Co, 1.0% Fe, and small amounts of C, S, B, Si, Mn and Cu.

Procedure

Weigh samples (see Table III) into 400-ml beakers. Weigh one blank for each different weight of sample taken. (The first ingot has no hafnium addition).

TABLE III

Hf range, %	0.01	0.05	0.1–0.5
Sample needed, *g*	1.0	0.5	0.1

A suitable sample (from 0.1 to 1.0 g) was dissolved in 15 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid on a hot plate. The solution was boiled after cautious addition of 2 g of ammonium persulphate in order to destroy carbides. Ten ml of 1 : 1 sulphuric acid (20 ml for a 1-g sample) were added and evaporated to strong fumes. The evaporation should be carried out slowly, since salts will precipitate and cause bumping if heated strongly. After cooling, about 75 ml of water were added and heated with stirring to dissolve salts. It was transferred to a mercury cathode for electrolysis at 15–20 amperes to a negative spot test for chromium. (Use a 200-ml volume for samples with 20 ml of 1:1 sulphuric acid, and 100 ml for all others). It was transferred to a hot plate, and boiled until all the yellow colour, if any, was discharged. After cooling, approximately 40 mg of titanium (titanium sulphate solution) were added to all samples and blanks weighing less than 0.5 g. It was adjusted to pH 8 to 9 by adding 1 : 1 ammonium hydroxide slowly, with stirring. It was gently boiled on a hot plate and the hydroxides allowed to settle to the bottom. The precipitate was filtered through a fast 11-cm paper (Whatman no. 41-H or S & S no. 589-1H), washed three times with hot 1 % ammonium nitrate, and dissolved into a 50-ml beaker with 25 ml of hot 0.8*N* perchloric acid. The filtrate was poured back through the paper into a 100-ml volumetric flask. The beaker and paper were washed with 0.8*N* perchloric acid to a total volume of 40 ml in the flask, making to volume with water. An aliquot of 20 ml was pipetted into a 25-ml volumetric flask. (Use a 10-ml aliquot if the hafnium is about 0.5 %). To it were added one ml of 1 % sodium chloride in 1 % thioglycollic acid and 3 ml of 0.05 % Xylenol Orange, and the solution was made to volume with water. (Made to volume with 0.3*N* perchloric acid if a 10-ml aliquot was used). The absorbance was measured at 535 mμ against a dye blank. Determine the amount of hafnium present from a calibration curve prepared under the similar conditions.

DISCUSSION

Since hafnium is a carbide-forming element, the destruction of all carbides in the solution procedure is imperative. Sodium sulphite and hydrogen peroxide were also tried as oxidizers, but the oxidation by these means was sometimes incomplete, thus necessitating a second treatment.

Electrolysis on the mercury cathode will remove iron and molybdenum, which interfere with the colour development, as well as nickel, cobalt, and chromium, which might disturb the absorbance measurement because of their intense colours. Sulphuric acid is preferable to perchloric acid as use of the latter greatly increases the time required for the complete deposition of chromium and molybdenum by mercury cathode.

Titanium peroxide reacted with ammonia to yield a greenish-black precipitate that was not easily soluble in 0.8*N* perchloric acid. This difficulty was eliminated by boiling to destroy the peroxy complex before the ammonia precipitation was made.

Hafnium in trace amounts will not be quantitatively precipitated from ammonia solution, and a suitable co-precipitant should be used. Fortunately, Udimet 500 contains about 3 % each of aluminium and titanium, which serve as carriers. For samples weighing less than 0.5 g, addition of extra titanium is necessary to precipitate all the hafnium.

TABLE IV. RECOVERY OF HAFNIUM IN NICKEL BASE ALLOY

% Hf Added	Sample, *g*	Aliquot used	Hf Taken, μg	Hf Found, μg	% Hf Recovered
0.01	1.0	20/100	106	102.5	96.7
0.01	1.0	20/100	106	117.5	110.8
0.05	0.5	20/100	265	245.0	92.5
0.10	0.1	20/100	106	102.5	96.7

Since sulphate interferes with the hafnium-Xylenol Orange colour development, this ammonia precipitation step would also serve the purpose of separation of sulphate. The ammonium nitrate serves to wash any excess sulphate out of the precipitate, and to prevent peptization.

Samples of Udimet 500, Heat no. 2-717-1 with addition of known amounts of hafnium were analyzed. The results are shown in Table IV. Reasonably good recoveries were obtained for the alloy containing 0.01 to 0.1% hafnium. Further study is needed of the analysis of samples containing over 0.25% hafnium because low recoveries have resulted by the method described here.

Acknowledgment—The author is indebted to Fran Warmuth for assistance during this study.

Zusammenfassung—Hafnium reagient ähnlich wie Zirkon mit Xylenol Orange. Der Hafnium Xylenol Orange Komplex weist fast übereinstimmende maximale Absorption mit dem Zirkon Xylenol Orange Komplex von 535 bis 540 mμ auf. Das Reagens zeigt eine empfindlichere Reaktion mit Hafnium als mit Zirkon. Die molare Absorption des Hafnium Xylenol Orange Komplexes wurde zu 48,700 bei 540 mμ bestimmt. Die Bildungskonstante des Hafnium Komplexes wurde auf 3,2 × 10^6 in 0,3*N* Perchlorsäure berechnet. Die Anwendungsbedingungen für Xylenol Orange als Reagens für die Hafniumbestimmung wurden untersucht. Nur Zirconium oder Hafnium geben eine purpur-rote Farbreaktion mit Xylenol Orange in 0,8*N* Perchlorsäure; dies bei Gegenwart von salzsäurem Hydroxylamin, welches Eisen sowie auch Wismuth abschirmt. Hafnium lässt sich von Zirkon leicht unterscheiden nachdem Zirkon durch Wasserstoffsuperoxid abgeschirmt werden kann. Beryllium kann als Demaskierungsreagens zur Bestimmung von Zirkon oder Hafnium in der Gegenwart von Fluoriden verwendet werden.

Résumé—Le hafnium réagit comme le zirconium avec le Xylénol Orange. Le complexe hafnium–Xylénol Orange présente un maximum d'absorption presque identique à celui du complexe zirconium-Xylénol Orange, vers 535–540 mμ. L'indicateur réagit avec plus de sensibilité avec le hafnium qu' avec le zirconium. On a trouvé l'absorption molaire du complexe hafnium–Xylénol Orange égale à 48,700 à 540 mμ. La constante de formation du complexe de hafnium a été calculée égale à 3,2 × 10^6 dàns l'acide perchlorique à 0,3*N*. On a étudié les conditions d'utilisation du Xylénol Orange comme indicateur pour l'analyse du hafnium. Seuls le zirconium et le hafnium donnent une couleur rouge pourpre par la réaction avec le Xylénol Orange dans l'acide perchlorique à 0,8*N*, en présence d'hydroxylamine chlorhydrique qui masque le fer et le bismuth. On peut distinguer le hafnium du zirconium, car le zirconium peut être masqué par l'eau oxygénée. On peut utiliser le beryllium comme agent de démasquage pour l'analyse du zirconium ou du hafnium, en présence de fluorures.

REFERENCES

[1] K. L. Cheng, *Talanta*, 1959, **2**, 61.
[2] *Idem*, *ibid.*, 1959, **2**, 186.
[3] *Idem*, *ibid.*, 1959, **2**, 266.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—I

THE BLOCKING OF INDICATORS AND ITS ELIMINATION

RUDOLF PŘIBIL
Laboratory of Analytical Chemistry, Chemical Institute,
Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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Summary—The formation with metallochromic indicators of complexes inert to substitution makes certain complexometric titrations impossible. The cations of bivalent copper, cobalt and nickel, in addition to others, show a tendency to form such complexes with for example Eriochrome Black T, Xylenol Orange, Methylthymol Blue. It has been proved that small quantities of *o*-phenanthroline entirely suppress this phenomenon, which is undesirable in complexometry. The presence of *o*-phenanthroline makes it possible reliably to determine copper as well as cobalt complexometrically against Xylenol Orange even at room temperature. The influence of *o*-phenanthroline is explained by the formation of substitution-labile complexes with copper or cobalt, and by the reaction mechanism at the point of equivalence. The influence of other materials on the colour change of the indicator in these titrations is also discussed.

VISUAL titration even in simple complexometric titrations is unfavourably influenced by a number of factors; for example, the high concentration of neutral salts (high ion strength of the solution), the development of intensely coloured complexes with the titrating agent during the titration (complexes of EDTA with Fe, Cu, Cr), or their slow formation at room temperature (Al–EDTA complex). The undesirable influence of neutral salts, as well as the original colour of the solution can to a considerable degree be decreased by dilution of the titrated solution; and the rapidity of the complex formation can be enhanced by increasing the temperature.

One of the most notable interferences in complexometry arises from the formation with the indicators of so-called substitution-stable complexes. In particular, cations with incomplete inner orbits as, for example, Fe^{3+}, Cr^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, tend to form complexes stable with respect to substitution. Such complexes prevent complexometric determination of these elements. Traces of them in the solution also may make it impossible to carry out entirely independent determinations or may have a very unfavourable influence on the colour change of the indicator. It is known, for example, that traces of copper or aluminium have an unfavourable influence on the complexometric determination of magnesium with Eriochrome Black T. Such phenomena often lead to an erroneous assessment of the suitability of a complexometric method.

Hitherto no effective remedy has been found against this undesirable phenomenon. For certain elements, of course, we can choose other indicators which do not form substitution-stable complexes. But such determinations can usually be carried out only in "pure solutions"; as, for example, the determination of copper or nickel with Murexide. In a number of cases we are dependent on the removal of these interfering elements by precipitation or masking in order to be able to determine other elements. (Screening of iron by triethanolamine, of copper by potassium cyanide, etc.) In fact, however, there exists a completely universal method which instead of preventing the formation of these substitution-stable complexes with the indicators, entirely suppresses their unfavourable influence. In this connection the following considerations are of importance:

The character of complexometric titration as an analytical method presupposes rapid reaction, at the most over several seconds. This applies to the principal complexometric reaction:

$$\mathrm{Me} + \mathrm{Y} = \mathrm{MeY} \qquad (1)$$

and also to the colour-indication replacement reaction:

$$\mathrm{MeI} + \mathrm{Y} = \mathrm{MeY} + \mathrm{I} \qquad (2)$$

(The ionic charges are omitted here for the sake of simplicity).

Indicators forming complexes which are labile with respect to substitution are reliably applicable in most complexometric titrations if they comply also with the other specific requirements (of sensitivity, etc.) Indicators forming complexes which are stable with respect to substitution are unsatisfactory principally on kinetic grounds (equation 2). In principle we can avoid this harmful influence if we substitute for the indication reaction (2) a different mechanism. Recently we described such a possibility in the complexometric determination of iron by Xylenol Orange.[1] In this the slow replacement-reaction of type (2) was substituted, on addition of ferrous salt, by the rapid redox reaction. A more universal method was found during investigation of certain screening agents. It consists in introducing a further complex-forming agent Z in a somewhat higher concentration than that of the indicator. This agent must have the following properties:

(a) Its reaction with the indicator complex

$$\mathrm{MeI} + \mathrm{Z} = \mathrm{MeZ} + \mathrm{I} \qquad (3)$$

must be rapid. That is possible especially if the auxiliary complex-forming agent Z has an electronic structure of different type from titrant used.

(b) The stability of the complex MeZ must, under the titration conditions, be approximately the same as the stability of the complex MeY.

If these conditions are fulfilled, the following reaction changes take place during the titration: at the beginning of the titration the solution contains free ions Me, the complex with indicator MeI, and complex MeZ. At first the concentration of Me decreases during the titration according to equation (1); then there follows the reaction:

$$\mathrm{MeZ} + \mathrm{Y} = \mathrm{MeY} + \mathrm{Z} \qquad (4)$$

and the liberated complex-forming agent Z then immediately reacts with the indicator complex MeI according to equation (3).

An example of this mechanism is the direct complexometric determination of copper against Xylenol Orange in the presence of a small amount of *o*-phenanthroline as an auxiliary complex-forming agent. Details are given in the Experimental Part.

EXPERIMENTAL

Preparation of standard solutions

The solution of 0.05 molar EDTA and the solutions of 0.05 molar $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Co(NO_3)_2$ were prepared by the usual method. Their concentration (titres) were determined complexometrically.

The solution of 0.001 molar *o*-phenanthroline was prepared by dissolution of the required quantity in re-distilled water. The solution of 0.01 molar *o*-phenanthroline was prepared in the same manner with moderate heat. The 0.05 molar solution was prepared by adding a small quantity of nitric acid.

Xylenol Orange, 0.2% aqueous solution.

Determination of copper

Since *o*-phenanthroline forms a quite stable complex with copper, it was necessary to ascertain the minimum amount which is necessary to accelerate the reaction at the equivalence point. For 100–300 ml of solution 0.5 ml of 0.001 molar solution gave a satisfactorily rapid and sharp colour change of Xylenol Orange in the titration with EDTA. The colour change depends on the concentration of copper as well as on that of the indicator. At low concentrations of copper (several mg) the colour change is from red-violet to yellow, and then to yellow-green. If the content of copper is 10 to 20 mg, the colour before the end-point of the titration is blue to violet and, on addition of 1 to 2 drops of EDTA, it changes to green-yellow. By the addition of 1 ml of 0.001 molar *o*-phenanthroline to the solution being titrated, the theoretical error is 0.003–0.05 ml of EDTA. This is negligible so that it is not necessary to prepare a solution of Cu-phenanthroline (Cu : Phen = 1 : 3) which has the same function as *o*-phenanthroline alone.

Procedure. To a slightly acid solution with at most 30 mg content of copper, add several drops of Xylenol Orange solution, and solid hexamethylenetetramine until a red or red-violet colour develops. Dilute with water to 200–250 ml, add 0.5 ml of 0.001 molar *o*-phenanthroline, and titrate with 0.05 molar EDTA solution to a yellow-green colour.

Determination of copper and lead

The procedure is the same as described above. Ascertain the total content of copper and lead by titration. Add excess of 0.1 molar phenanthroline and after three minutes titrate the liberated EDTA[2] with the solution of 0.05 molar $Pb(NO_3)_2$.

Determination of cobalt

The procedure is the same as that described for the determination of copper. A very sharp colour change is obtained if the titration is carried out at 50°.

The results of the determinations using the procedures here described agreed with other complexometric methods and therefore it is not necessary to give them in tabular form.

DISCUSSION

This example of direct complexometric determination of copper against Xylenol Orange, in the presence of small concentrations of *o*-phenanthroline as an auxiliary complex-forming agent, illustrates how it is possible to eliminate the influence of the formation of substitution—inert indicator complexes. In this case it was proved that the cation $Cu(Phen)_3^{2+}$, bonded in a complex, participates in the indication mechanism at the equivalence point. This cation develops just before the end-point of the titration according to the equation:

$$3Cu(Phen)^{2+} + 2H_2Y^{2-} = 2CuY^{2-} + Cu(Phen)_3^{2+} + 4H^+$$

and is sufficiently labile to substitution in practice to react immediately with EDTA.

Should the principle described in this paper by the equations (3) and (4) be of general validity, we may expect that there exist other compounds whose structure will permit a similar "indicator effect" with other cations with incomplete inner orbits. Further experiments have indicated that this does not only concern compounds which form insoluble complexes. Thus, for example, sodium diethyldithiocarbaminate or cupferron[3] have a similar, if not so marked, influence in the determination of copper here described. In the titration of cobalt against Xylenol Orange the addition of acetylacetone showed a favourable influence. In a similar titration of nickel this effect has not so far been observed although a range of complex-forming substances have been tested. This may be explained by the especially high inactivity of the indicator complex of nickel.

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Zusammenfassung—Die Bildung äusserst reaktionsträger Metallkomplexe mancher metallochromer Indicatoren macht einige komplexometrische Titrationen unmöglich. Von den in Frage kommenden Kationen zeigen die zweiwertigen Ionen von Kupfer, Cobalt und Nickel besonders starke Tendenzen zur Blockierung von z.B. Eriochromschwarz T, Xylenolorange und Methylthymolblau. Es wurde gefunden, dass die Zugabe kleiner Mengen von *o*-Phenanthrolin das störende Blockieren vollständig unterdrückt. In Anwesenheit kleiner Mengen von *o*-Phenanthrolin wird die Titration von Kupfer (II) und Cobalt (II) mit EDTA unter Verwendung von Xylenolorange als Indicator selbst bei Zimmertemperatur möglich. Als Erklärung für die Wirksamkeit des Phenanthrolins wird die Bildung hochaktiver "Hilfskomplexe" gegeben, die (als Zwischenprodukte wirkend) auf die Endpunkstreaktion einen beschleunigenden Einfluss haben. Der Einfluss auch anderer Substanzen auf den Farbwechsel der Indicatoren in derartigen Titrationen wird diskutiert.

Résumé—La formation de quelques complexes de substitution inertes avec des indicateurs colorés de cations métalliques rend impossible un certain nombre de titrages complexométriques. Entre autres cations, le cuivre divalent, le cobalt, et le nickel ont tendance à former de tels complexes avec, par exemple, le noir ériochrome T l'orangé de xylénol, le bleu de méthylthymol. On a montré que de petites quantités d'*o*-phénanthroline suppriment entièrement ce phénomène qui est indésirable en complexométrie. La présence d'*o*-phenanthroline permet de déterminer en toute sécurité, à la fois le cuivre et le cobalt avec l'orangé de xylénol, même à la température ambiante. L'influence de l'*o*-phenanthroline s'explique par la formation de complexes de substitution labiles avec le cuivre ou le cobalt et par le mécanisme de la réaction au point équivalent. L'influence d'autres substances sur le changement de couleur de l'indicateur dans ces titrages est aussi discutée.

REFERENCES

[1] F. Vydra, R. Přibil and J. Körbl, *Talanta*, 1959, **2**, 311.
[2] R. Přibil and F. Vydra, *Coll. Czech. Chem. Communs.* In press.
[3] G. Svehla. Private communication.

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2-MERCAPTOACETIC (THIOGLYCOLLIC) ACID AS A REAGENT FOR ZIRCONIUM

SUSEELA B. SANT*
Carr Laboratory, Mount Holyoke College, South Hadley, Mass., U.S.A.
and
BHARAT R. SANT*
Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La., U.S.A.

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Summary—Thioglycollic acid has been shown to be a suitable reagent for the quantitative precipitation of zirconium at a pH of about 4.5. A basic zirconyl thioglycollate is formed and therefore the analysis is completed by weighing the zirconium oxide. Interference due to several metal ions is discussed.

RECENTLY we reported the use of thiodiglycollic acid, $S(CH_2COOH)_2$, as a suitable reagent for zirconium.[1] Preliminary experiments showed that under suitable conditions zirconium can be quantitatively precipitated by 2-mercaptoacetic (or thioglycollic) acid. While this reagent is a well known complexing agent,[2,3] no information seems to exist on its use as a precipitant for zirconium. The present communication describes optimum conditions for the determination of zirconium by thioglycollic acid. Interference due to other metal ions is also discussed.

EXPERIMENTAL

Reagents

Reagent grade zirconyl nitrate was used to prepare its solution in water. The acidity with respect to nitric acid in it was maintained at $0.2N$ and the zirconium content was determined by the *m*-nitrobenzoic acid method.[4] Evans' thioglycollic acid, $HS—CH_2COOH$, of 98–99% assay was used without further purification as a 5% aqueous solution.

Procedure

To an aliquot portion of zirconyl nitrate solution diluted to about 150 ml, 10–15 ml of 5% thioglycollic acid and methyl orange indicator were added. A 10% solution of ammonium acetate was now added so as to raise the pH of the system to about 4.5. The system was heated on a hot plate at 85–90° for nearly 15 minutes and the white precipitate filtered after an hour. It was washed with a 5% ammonium nitrate solution, dried, ignited and eventually weighed as ZrO_2.

RESULTS AND DISCUSSION

Results entered in Table I show a fair agreement between the experimental values and those expected on the basis of the standard *m*-nitrobenzoic acid method.

Under the given experimental conditions, alkaline earth metal ions, manganese^{II}, magnesium, beryllium, aluminium, cerium^{III}, lanthanons, chromium^{III}, and iron^{III} do not interfere in the present method of estimating zirconium. Under the same experimental conditions, vanadyl and uranyl ions give with thioglycollic acid blue and orange colours respectively without, however, affecting the accuracy of the results. Tin^{II}, mercury^{II}, zinc, cadmium, titanium^{IV} and thorium give white precipitates, copper^{II} a violet precipitate, lead^{II} a yellow precipitate and nickel^{II} a dirty coloured precipitate. Although cobalt^{II} and bismuth^{III} produce only brown colours with thioglycollic acid, these, in presence of zirconium, are co-precipitated

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* Present address: Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

appreciably. The above interfering metal ions should therefore be either absent or previously removed.

TABLE I. DETERMINATION OF ZIRCONIUM BY THIOGLYCOLLIC ACID

ZrO_2, *g*		Difference
By *m*-nitrobenzoic acid	By thioglycollic acid	
0.01770	0.01776	0.00006
0.04425	0.04420	0.00005
0.08850	0.08860	0.0001
0.1327	0.1328	0.0001
0.1770	0.1772	0.0002
0.2212	0.2213	0.0001

The composition of the zirconium complex varies somewhat, but corresponds approximately to a basic salt with the formula

$$ZrO(OH)\cdot CH_2SH\cdot COO.$$

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Zusammenfassung—Thioglykolsaure wurde als geeignetes Fällungsmittel zur quantitativen Niederschlagung von Zirkonium bei pH ca 4.5 gefunden. Ein basisches Zirkonylthioglykolat wird gebildet und daher die Analyse durch Verglühen zu Zirkoniumoxyd abgeschlossen. Störungen durch verschiedene Metallionen werden diskutiert.

Résumé—Les auteurs ont montré que l'acide thioglycollique est un réactif converable pour la précipitation quantitative du zirconium à un pH d'environ 4,5. Il se forme un thioglycollate de zirconyl basique, on complète donc l'analyse par pesée de l'oxyde de zirconium. L'interférence due à différents ions métalliques est discutée.

REFERENCES

[1] S. B. Sant and B. R. Sant, *Analyt. Chim. Acta*, in press.
[2] I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Volume III, Interscience Publishers, New York, 1958, p. 391.
[3] D. L. Leussing, *J. Amer. Chem. Soc.*, 1958, **80**, 4180.
[4] R. Belcher and C. L. Wilson, *New Methods in Analytical Chemistry*, Chapman and Hall, London, 1955, p. 3.

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ÜBER DAS VERHALTEN VON ISOLIERTEN EINSCHLÜSSEN AUS EISENWERKSTOFFEN BEI HOHEN TEMPERATUREN

HANNS MALISSA*
Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

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Allgemeines über Probekörper und Schmelzen—Erhitzungsverhalten von Eisen-Mangan-Silikatschlacken in Luft und Argon—Isolate aus Transformatorenblechen und unberuhigten Weicheisenschmelzen.

Zusammenfassung—Es wird an einigen Beispielen gezeigt, dass ein Erhitzungsmikroskop sehr gut zum Studium des Schmelzverhaltens isolierter oxydierter Gefügebestandteile herangezogen werden kann.

WIE in der organischen und pharmazeutischen Industrie die Schmelzpunktsbestimmung sowie andere thermoanalytische Untersuchungen neben der chemischen Analyse ein wesentliches Kriterium der Reinheitsprüfung und Identifizierung bilden, so sollte auch bei der metallkundlichen Analyse[1] neben den bisherigen Analysendaten als ein weiteres auch das Verhalten der isolierten Körper bei hohen Temperaturen näher untersucht und beschrieben werden. Weder die chemische noch die Strukturanalyse erlauben sichere Rückschlüsse auf das Schmelzverhalten eines bestimmten isolierten Oxydkörpers. Aus der Übertragung der Analysenergebnisse in bekannte Drei- und Vielstoffsysteme kann man zwar mit einiger Sicherheit auf das Verhalten während des Schmelzens schliessen. Die Untersuchung isolierte Körper in inerter, oxydierender oder reduzierender Gasatmosphäre kann hier Fortschritte bringen.

Im Schrifttum sind speziell für die Untersuchung von Kohle- und Koksaschen zahlreiche Verfahren vorgeschlagen und in Verwendung.[2] Hier soll als erste Stufe des Studiums isolierter Produkte bei hohen Temperaturen die Verwendung eines Erhitzungsmikroskops betrachtet werden. Vorweggenommen sei aber, dass die hier skizzierte Arbeitsmethode noch nicht die Endlösung für metallkundliche Zwecke darstellt, dass wir aber an einer solchen arbeiten.

Um das Verhalten der Probekörper bei hohen Temperaturen soweit als möglich ausschöpfen zu können, kommt nur ein Verfahren in Frage, das neben einer subjektiven auch eine objektive registrierende Beobachtung und dies sowohl im Auf- als auch Durchlicht und im polarisierten Licht gestattet.

Der Probekörper

Wie die Untersuchungen von W. Radmacher[2] gezeigt haben, kommt der Form des Probekörpers eine besondere Bedeutung zu. Leider sind wir in den meisten Fällen nicht in der Lage, bestimmte, einheitliche Probekörper herzustellen, sondern müssen uns mit den aus der verfügbaren Menge herstellbaren begnügen. Oft aber interessiert gerade ein besonders ausgebildetes (verformtes) Teilchen.[3]

Radmacher hat vier verschiedene Probekörper—zylindrische, würfelförmige sowie symmetrische und unsymmetrische, pyramidenförmige—wie sie nach den

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* Neüe Anschrift; *Institüt für analytische Chemie der Technischen Hochschüle Wien, Wien VI, Getreidemarkt 9, Austria.*

Normverfahren zur Asche-Schmelzpunktsbestimmung gefordert werden, untersucht und gefunden, dass, je grösser der Probekörper ist, der Temperaturanstieg um so geringer sein muss. Ein Segerkegel z.B. hatte schon weitgehend seine Form verändert, während an anderen, aus dem gleichen Material mit der gleichen Menge hergestellten zylindrischen Probekörpern noch keine merkliche Änderung festzustellen war. Er kommt zu dem Schluss, dass der zweckmässigste Probekörper für die Aschenanalyse ein Zylinder von 7 mm ϕ und 7 mm Höhe ist oder ein Würfel von 7 mm Kantenlänge. Für derartige Körper ist ein durchschnittlicher Materialbedarf von 300 mg angegeben, eine Menge, die bei der metallkundlichen Analyse nur selten anfällt. Wenn 10 mg Substanz für diesen Zweck zur Verfügung stehen, so wird mit Hilfe eines kleinen Gesenkes ein zylindrischer Pressling (etwa 10–15 kg/mm^2 Pressdruck) hergestellt, der 1 mm ϕ und 1–3 mm Höhe aufweist. Die zylindrische Probenform ist der würfelförmigen vorzuziehen, da keine Gefahr der verkanteten Aufstellung besteht und evtl. Flächenmessungen (Volummessungen) leichter durchgeführt werden können. Jedoch kommt dieser Art der Probekörperherstellung zunächst noch geringe Bedeutung zu, da wir selten über soviel Material verfügen und da oft das Verhalten eines einzelnen, ganz bestimmten Körpers interessant ist.

Das *Erhitzungsmikroskop* sowie dessen Bedienung ist in seinen Einzelheiten ausführlich beschrieben worden,[2] so dass sich hier ein weiteres Eingehen darauf erübrigt, da deine wesentlichen Änderungen vorgenommen werden.

Wichtiger ist nach den bisherigen Untersuchungen, einiges zur *Begriffsbestimmung* während des Erhitzens zu sagen, um zum Verständnis der charakteristischen Temperaturpunkte oder -bereiche, die ja auch für den physikalischen Zustand der Probe verantwortlich sind, beizutragen. Es sollen hier in Anlehnung an Radmacher folgende Begriffe gelten:

(1) Der Formänderungspunkt (-bereich) ist jene Temperatur, bei der das erste merkbare Anzeichen einer Formänderung, Abrundung der Kanten, Aufblähen, Veränderung der Oberfläche, Änderung der Farbe oder Durchsichtigkeit usw. eintritt.

(2) Erweichungs- bzw. Sinterungspunkt (-bereich) ist der Punkt (Bereich), an dem der Probekörper *sichtlich* seine Gestalt verliert.

(3) Schmelzpunkt bzw. -bereich ist die Temperatur, bei der die Probe vollständig ihre Form verliert und zu einer mehr oder minder kugeligen Form (Halbkugel, Kugelsegment (s. Bild 3), stehendem oder hängendem Tropfen (s. Bild 5) zusammengeflossen ist.

(4) Fliesspunkt bzw. -bereich ist die Temperatur, bei der sich der Probekörper—natürlich abhängig von Form und Natur seiner Unterlage—gleichmässig ausbreitet, s. Bild 1 rechts oben (Fliesskegel), Bild 3 rechts oben, Bild 5 oben, Bild 6 rechts unten.

Im übrigen sei aber hier darauf hingewiesen, dass die Frage der Schmelzdefinitionen sicher noch einer Diskussion unterworfen sein wird, denn grundsätzlich gibt es bei homogenen Körpern nur einen Punkt, den Schmelzpunkt, und der ist abhängig von der Einheitlichkeit und Reinheit der Verbindung. Besser erfassbar erscheint dieser Punkt dann, wenn z.B. ein anisotroper Körper vollkommen isotrop geworden ist. Wann und ob dies bei den bei der metallkundlichen Analyse anfallenden Proben der Fall bzw. erfassbar ist, bedarf noch der weiteren Untersuchung, ebenso wie die Gleichsetzung des Schmelzverhaltens eines Körpers im Erhitzungsmikroskop mit seinem Verhalten im flüssigen bzw. heissen Metallbad.

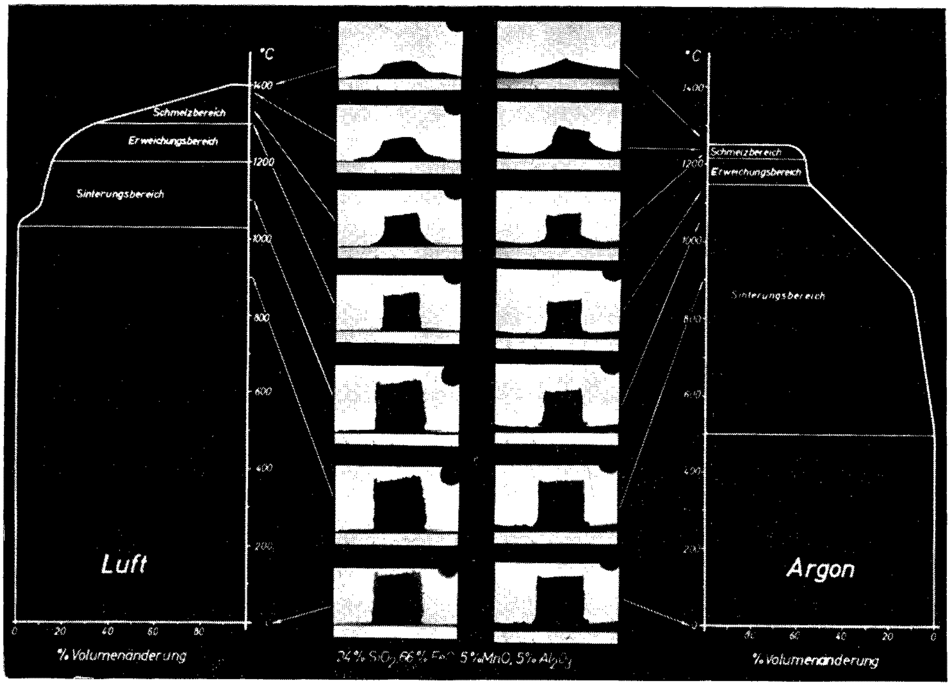
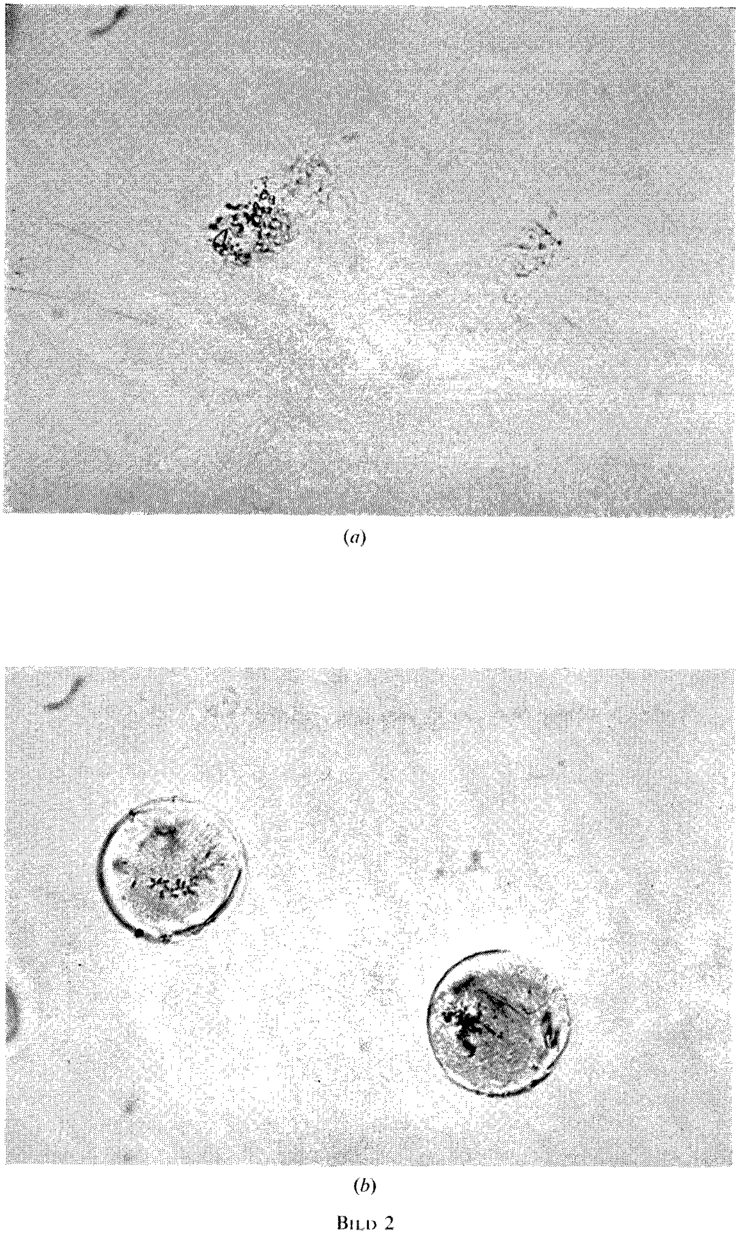


BILD 1: Schmelzverhalten von Eisen–Mangan–Silikateinschlüssen aus einem Puddeleisen.



(*a*)

(*b*)

Bild 2

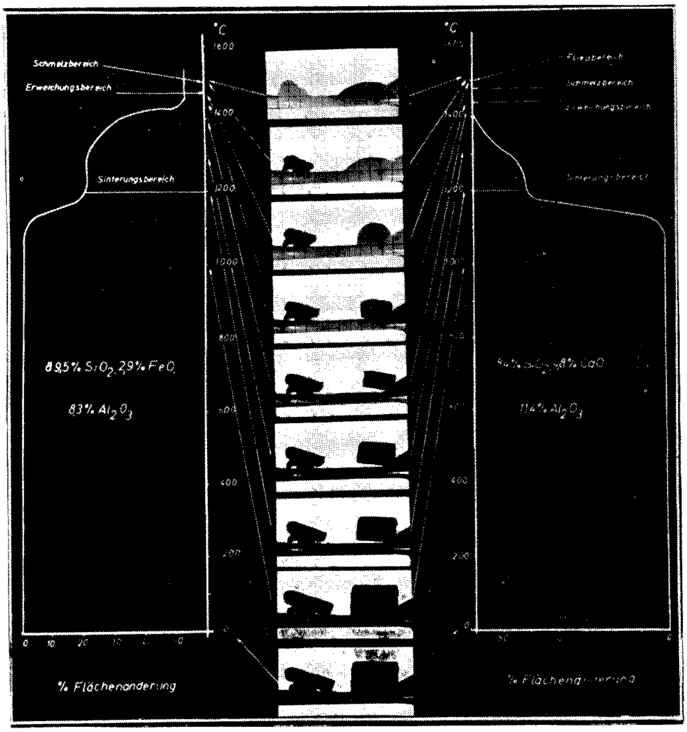
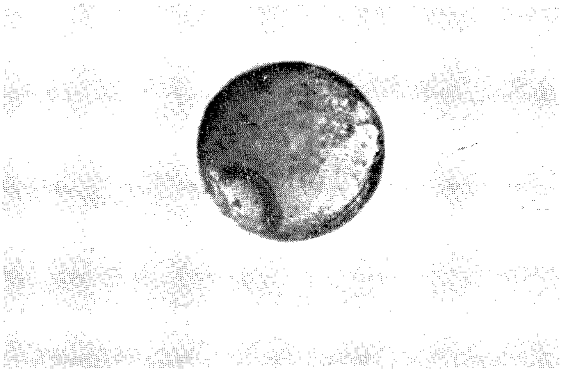
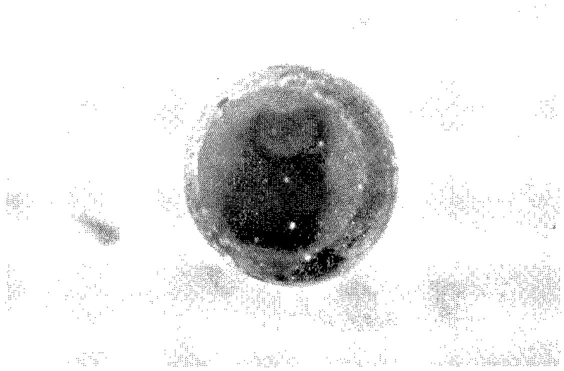


BILD 3: Schmelzverhalten von Einschlüssen aus Transformatorenblechen.



(*a*) Isolat C 50 : 1



(*b*) Isolat D 50 : 1

Bild 4: Anschliffe von durchsichtigen (Isolat C) und undurchsichtigen (Isolat D) Schlackenkugeln.

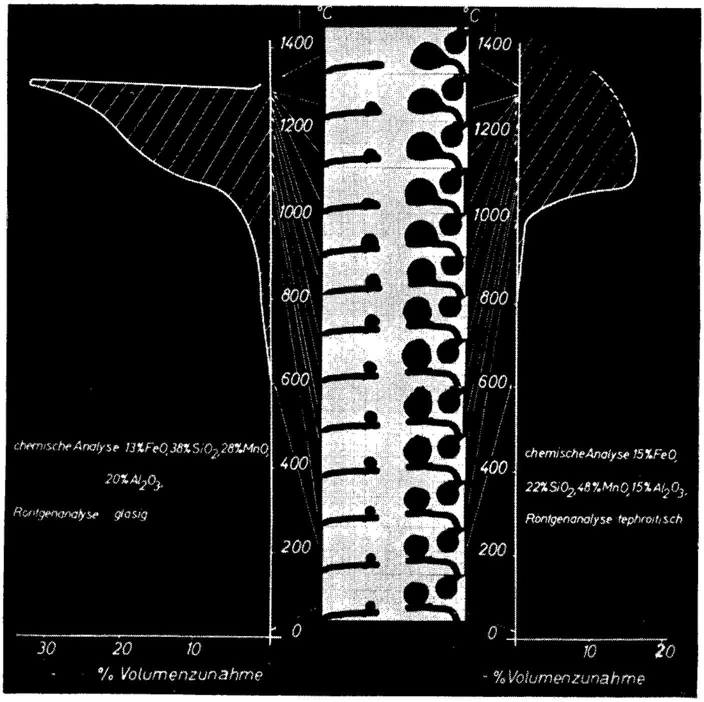


BILD 5: Schmelzverhalten isolierter Schlackenkugeln.

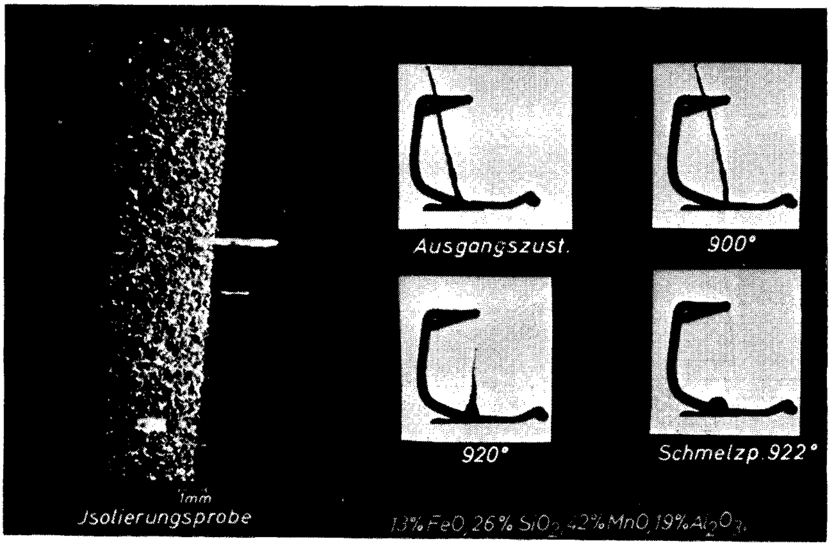


BILD 6

Jedoch lassen die Ergebnisse zusammen mit anderen Daten—wie an einzelnen Beispielen gezeigt werden soll, trotzdem Aussagen über wahrscheinlichen Flüssigkeits- und Verformbarkeitsgrad zu. An einigen Beispielen soll über die Schmelzpunktsbestimmung diskutiert werden.

(1) *Ein Isolat aus einem Puddeleisen:* dessen chemische Analyse wie folgt lautet: 24% SiO_2, 5% Al_2O_3, 5% MnO, 66% FeO und Spuren von CaO und MgO zeigte bei der mikroskopischen Betrachtung viele kristallisierte, doppelbrechende und wenige glasige, schwach braun gefärbte Kristalle. Da genügend Probematerial zur Verfügung stand', wurden zwei würfelförmige Presslinge von etwa 2 mm Kantenlänge angefertigt und einmal an Luft und zum anderen in Argon im Erhitzungsmikroskop bei einer durchschnittlichen Temperatursteigerung von etwa 5°/min bis 1000°C und von da an mit 2 bis 3°/min bis zum Schmelzpunkt erhitzt. Es gibt sich ein deutlicher Einfluss der herrschenden Atmosphäre zu erkennen, wie dies sowohl im Bild 1 als auch in Tafel 1 zu sehen ist.

TAFEL 1.

Temperatur °C	scheinbare Volumenänderung			
	Luft		Argon	
	%	Bemerkung	%	Bemerkung
20	0		0	
500	0		0	
900	0		10	Sinterung
1000	0		20	Sinterung
1060	0		42	Sinterung
1100	8	Sinterung	46	Sinterung
1150	8	Sinterung	50	Erweichung
1195	8	Sinterung	54	Erweichung
1200	15	Erweichung	54	Erweichung
1230	15	Erweichung	56	Schmelzen
1235	15	Erweichung	63	Schmelzen
1238	18	Erweichung	65	Schmelzen
1240	18	Erweichung	75	Schmelzen
1243	18	Erweichung	84	Schmelzen
1245	18	Erweichung	87	Schmelzen
1300	43	Erweichung		
1330	67	Schmelzen		
1380	77	Schmelzen		
1390	84	Schmelzen		

Fasst man die charakteristischen Temperaturbereiche zusammen, wie dies in Tafel 2 geschehen ist, so ergibt sich folgendes: Alle charakteristischen Bereiche (Sinterung, Erweichung und Schmelzen) beginnen beim Erhitzen an Luft bei wesentlich höherer Temperatur und—was wichtiger erscheint—der Erweichungs- und Schmelzbereich zieht sich über einen breiten Temperaturintervall hin, während gerade diese wichtigen Bereiche in Argonatmosphäre geringer und ausgeprägter sind und daher auch besser erfasst werden können.

(2) *Isolate aus Transformatorenblechen:* Die chemische Analyse war folgende:

Isolat A: 84% SiO_2, 11,4% Al_2O_3, 4,8% CaO; FeO, MgO und $TiO_2 \leqslant 1\%$
Isolat B: 89,5% SiO_2, 8,3% Al_2O_3, 2,9% FeO; CaO, MgO und $TiO_2 \leqslant 1\%$

TAFEL 2.

Atmosphäre	Sinterung °C	Erweichung °C	Schmelzen °C
Luft	1100–1200	1200–1330	1330–1390
Argon	900–1150	1150–1230	1230–1245

Die Röntgenanalyse ergab in beiden Fällen glasige, wenig kristallisierte Körper. Die mikroskopische Untersuchung zeigte ebenfalls vorwiegend glasige Körper, in denen kristallisierte Substanzen entahalten sind, wobei noch bemerkenswert ist, dass —wie Bild 2 zeigt—das Isolat A vorwiegend eckige Kristalle liefert und das Isolat B kugelige.

Da von jeder dieser Proben nur einige Milligramme zur Verfügung standen, konnte keiner der empfohlenen Prüfkörper hergestellt werden. Mit Hilfe eines kleinen Gesenkes, ähnlich wie in der Spektralanalyse verwendet, konnten aus dem Isolat A durch Handdruck ein Quader von 2 mm^2 Grundfläche und 1,3 mm Höhe und vom Isolat B ein solcher mit einer Grundfläche von ebenfalls 2 mm^2 und einer Höhe von lediglich 0,5 mm hergestellt werden.

Das Verhalten dieser beiden Prüfkörper beim Erhitzen im Erhitzungsmikroskop and der Luft zeigt Bild 3. Demnach verhalten sich die beiden Substanzen trotz sehr ähnlicher Silizium- und Aluminiumgehalte keinesfalls gleich, da einmal die prozentuale Volumverminderung wesentlich unterschiedlich ist, zum anderen die Sinterbereiche beim Isolat A in einem Intervall von 200°C, beginnend bei 1200°C, beim Isolat B in einem solchen von 400°C mit dem Beginn bei 1000°C liegen. Der Erweichungsbereich liegt bei Probe A innerhalb 40, bei B innerhalb 110°C. Der Schmelzbereich liegt, wie dies auch Tafel 3 zeigt, zwischen 1440 und 1500°C innerhalb 60°C, bei Probe A wesentlich geringer als der für die Probe B, der zwischen 1510 bis 1540°C im Bereich von 30° wesentlich höher liegt. Das heisst, die kalziumoxydhaltigen, eckigen Kristalle zeigen gegenüber den kalziumoxydfreien, aber eisenoxydhaltigen, kugelförmigen Verbindungen einen niedrigeren Schmelzpunkt.

TAFEL 3.

Isolat	Sinterung °C	Erweichung °C	Schmelzen °C
A	1200–1400	1400–1440	1440–1500
B	1000–1400	1400–1510	1510–1540

Es sei an dieser Stelle hervorgehoben, dass sicherlich die während des Erhitzens erhaltenen Zahlen von der Korngrösse des Produktes und vom Pressdruck, den der

Körper erfahren hat, sowie von den den Körper umgebenden atmosphärischen Bedingungen abhängen.

Trägt man die Analysenwerte vom Isolat A in das Dreistoffsystem SiO_2—CaO—Al_2O_3 ein, so stimmt der Schmelzpunkt von etwa 1460° sehr gut mit der eutektischen Rinne überein. Die chemische Analyse des Isolates B muss naturgemäss in das Dreistoffsystem SiO_2—FeO—Al_2O_3 eingetragen werden, und man liegt damit in der Phasengrenzfläche zwischen Cristobalit und Mullit, wobei schon sehr geringe Mengen von FeO den Schmelzpunkt von ca. 1600° auf 1510° herunterdrücken. Dies stimmt mit dem Verlauf der Schmelzrinne gut überein.

(3) *Isolate aus unberuhigten Weichstählen:*[3] Die chemische Zusammensetzung war folgende:

Isolat C: 38% SiO_2, 20% Al_2O_3, 28% MnO, 13% FeO

Isolat D: 22% SiO_2, 15% Al_2O_3, 48% MnO, 15% FeO

Die Röntgenanalyse zeigte für C einen kristallisierten Körper, der nach der Textur des Diagramms dem Tephroit zugeordnet werden kann, während D auf einen glasigen Körper hinweist. Die mikroskopischen Analysen der Isolate zeigen durchsichtige und undurchsichtige, braunschwarze, mitunter Hohlräume (Isolat C) aufweisende Kugeln, die im Anschliff, wie Bild 4 zeigt, im Innern entweder Blasen oder Auskristallisationen (Isolat D) beinhalten.

Das Verhalten derartiger Kugeln im Erhitzungsmikroskop geht aus Bild 5 hervor. Diese Kugeln wurden auf einen aus dünnem Platindraht hergestellten Träger gebracht und nebeneinander in das Mikroskop eingesetzt. Während des Erhitzens verhielt sich die durchsichtige Kugel wesentlich anders als die undurchsichtige, und zwar derart, dass sie oberhalb 400°C ihre Durchsichtigkeit verlor, bei etwa 800°C sich aufzublähen begann, bei 1230°C unter kräftiger Volumzunahme zu schmelzen begann und bei 1260°C den Schmelzpunkt erreichte. Unmittelbar darauf erfolgte ein nahezu vollständiger Zusammenbruch des Probekörpers, um bei 1300°C eine neuerliche, wenn auch geringere Aufblähung zu erfahren und um bei 1340°C neuerlich und vollständig zusammenzubrechen. Die undurchsichtigen Kugeln hingegen begannen erst bei über 1000°C sich aufzublähen, wiesen an und für sich eine wesentlich geringere prozentuale Volumzunahme auf, erreichter aber bei der gleichen Temperatur wie die durchsichtigen Kugeln ihren Schmelzpunkt, wurden dann ohne wesentliche Volumänderung dünnflüssig und sackte langsam durch die Öse des Platindrahtes durch. Wieweit ein derartiges Verhalten mit der Viskosität dieser Kugel in Zusammenhang steht und daraus rückschliessend das Verhalten der Kugeln im Schmelzfluss beurteilt werden darf, muss späteren Untersuchungen vorbehalten bleiben. Hier können die Arbeiten von F. Johannsen und W. Wiese[4] wertvolle Hinweise geben.

(4) Ein weiteres interessantes Beispiel einer Schmelzpunktsbestimmung zeigt Bild 6, in dem auf der linken Bildseite eine Isolierungsprobe mit nadelförmigen Einschlüssen zu sehen ist, deren chemische Analyse wie folgt lautet: 13% FeO, 26% SiO_2, 42% MnO und 19% Al_2O_3. Das Röntgendiagramm zeigte wiederum den tephroitartigen Charakter der Einschlüsse und der Schmelzpunkt einer einzelnen Nadel, der auf 2°C genau erfassbar war, lag bei 922°C, wobei die Erweichung bei 900°C erfolgte. In diesem Falle wurde aus dem Gesamtisolat mit Hilfe des

Mikromanipulators[5] eine Nadel ausgesucht und diese, wie im Bild 6, Mitte oben (Ausgangszustand), zu sehen ist, schräg durch den Platindrahthalter gesteckt.

Überträgt man die chemische Analyse in vereinfachter Weise in das Dreistoffsystem MnO—FeO—SiO_2, wobei Aluminiumoxyd und Siliziumdioxyd addiert werden, so kommt man in ein Gebiet mit Schmelzpunkten von 1200°C. Überträgt man aber die chemische Analyse in das Dreistoffsystem MnO—Al_2O_3—SiO_2 unter Zusammenfassung von FeO und MnO, so kommt man in ein Gebiet, welches im reinen Dreistoffsystem Schmelzpunkte von etwa 1140°C aufweist, so dass man sehr wohl im Vierstoffsystem einen noch niedrigeren Schmelzpunkt erwarten darf. Es steht auf alle Fälle fest, dass sich Körper, die bei 900°C erweichen und bei 920°C schmelzen, sehr wohl beim Walzen verformen[3] lassen.

Summary—The value of a heating microscope for the investigation of the melting behaviour of isolated oxidised structural components in ferrous materials is illustrated by examples.

Résumé—On illustre par des exemples l'intérèt du microscope chauffant pour l'étude de la fusion de composés isolés à l'état oxydé dans des matériaux ferreux.

SCHRIFTTUM

[1] P. Klinger u. W. Koch, *Beiträge zur metallkundlichen Analyse.* Verlag Stahleisen m.b.H., Düsseldorf, 1949.

[2] W. Radmacher, *Brennstoff-Chemie* 1949, **21/22,** 377.

[3] H. Lessing u. H. Malissa, *Arch. Eisenhüttenwes.*, 1958, **29,** 627.

[4] F. Johannsen u. W. Wiese, *Erzmetall,* 1958, **19,** 1.

[5] W. Koch, H. Malissa u. D. Ditges, *Arch. Eisenhüttenwes.*, 1957, **28,** 785.

Talanta, 1959, Vol. 3, pp. 103 to 104. Pergamon Press Ltd. Printed in Northern Ireland

PRELIMINARY COMMUNICATION

New redox systems—I. Oxidation of bivalent cobalt with iron^{III} chloride in 1:10-phenanthroline solutions

(*Received* 12 *September* 1959)

In the study of the properties of ferric iron and of bivalent and tervalent cobalt with 1:10 phenanthroline a reaction of considerable theoretical interest has been observed. In a weakly acid solution of bivalent cobalt and ferric salt (optimum pH 3), on addition of 1:10 phenanthroline solution, the tervalent iron is reduced to the bivalent state which is simultaneously bound by the phenanthroline present to form the intensely red ferroïn complex. This colour reaction, which can be used for the very sensitive detection of cobalt, arises only because of the existence of phenanthroline complexes of iron and cobalt in both valency states, with stability constants which permit the reaction.

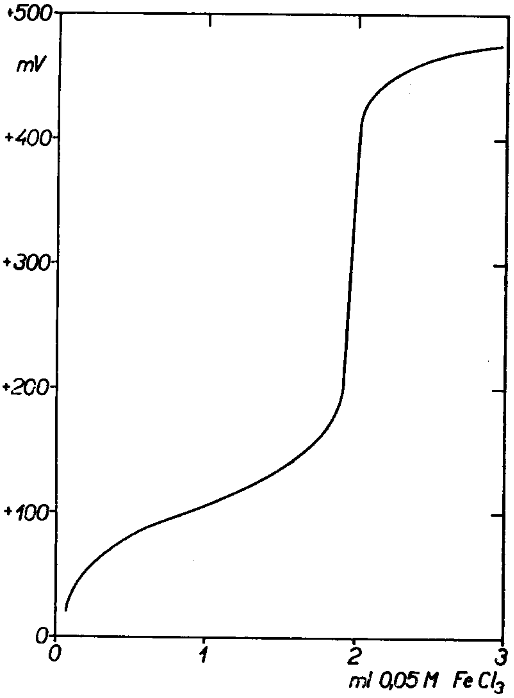


Fig. 1

2 ml of 0·05*M* Co
25 ml of 0·05*M* 1:10-phenanthroline
20 ml of buffer (formic acid with ammonium formate, pH 3)
Titrated with 0·05*M* $FeCl_3$; Pt electrode and saturated calomel electrode.

The redox character of the reaction was verified by potentiometric titration of a solution containing cobaltous salt and 1:10-phenanthroline with 0·05*M* ferric chloride. The titration curve and the appropriate data are given in Fig. 1. The reaction is rapid and quantitative at pH 3. The redox potential for the couple

$$\mathrm{Co^{II}(Phen)_3Cl_2 + Cl^- = Co^{III}(Phen)_3Cl_3 + e}$$

was determined by analysis of the potentiometric curve and the value 0·38 V found, in excellent agreement with the value 0·37 V reported by Paglia and Sironi[1] for these complexes prepared synthetically.

The reaction was also followed spectrophotometrically and found to be stoichiometric provided the ratio of phenanthroline to total iron plus cobalt was at least 6 to 1. From the known composition of all the complexes concerned, the reaction can be formulated as

$$\mathrm{[Fe_2(Phen)_4(OH)_2]^{2+} + 2Co(Phen)_3{}^{2+} + 2HPhen^+ \rightleftharpoons 2Fe(Phen)_3{}^{2+} + 2Co(Phen)_3{}^{3+} + 2H_2O}$$

(Tervalent iron forms with 1:10-phenanthroline in acid solution a binuclear complex of different composition from the complexes of other metals.[2,3])

Analytical applications

Preliminary tests show that the reaction can be used for the highly selective oxidimetric determination of cobalt. The end-point can be detected potentiometrically or spectrophotometrically. Traces of cobalt—several μg per ml—can be indirectly determined colorimetrically as ferroïn. In solutions coloured by ions such as Ni or Cr, the ferroïn produced in the reaction can be extracted as its perchlorate with chloroform or nitrobenzene and then determined colorimetrically.[4]

The reaction is being further studied in its theoretical as well as its analytical aspects and the results will be published in this journal.

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Czechoslovak Academy of Science
Chemical Institute, Laboratory of Analytical Chemistry
Prague, Czechoslovakia

F. Vydra
R. Přibil

REFERENCES

[1] E. Paglia and C. Sironi, *Gazz. chim. Ital.*, 1957, **87**, 1125.
[2] A. Gaines Jr., L. P. Hammett and G. H. Walden Jr., *J. Amer. Chem. Soc.*, 1936, **58**, 1668.
[3] C. M. Harris and T. N. Lockyer, *Chem. and Ind.*, 1958, 1231.
[4] B. W. Margerum and C. V. Banks, *Analyt. Chem.*, 1954, **26**, 200.

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SHORT COMMUNICATIONS

Vereinfachte Schnellmethode zur Sulfatbestimmung durch Ionenaustausch

(*Received* 20 *April* 1959)

Es wurden Austauschadsorbentien seit langem zur Sulfatanalyse verwendet, Grössten Teils dienen sie zur Beseitigung der störenden Komponenten. So verfährt auch Bahrdt[1] in seiner Schnellmethode, indem er den Sulfatgehalt von Naturwässern mit bestimmter Menge einer $BaCl_2$ Lösung versätzt, und den Überschuss von $BaCl_2$ mit K-Palmitat titriert. Da Ca und Mg bei der $BaSO_4$-Abscheidung stören, wird die zu analysierende Lösung durch eine Na-Permutit-Säule filtriert. Unabhängig von Bahrdt, aber in ähnlicher Weise arbeiten Kehren und Stommel.[2]

Die gravimetrische Bestimmung von $BaSO_4$ Niederschläge wird durch manche Ionen gestört, so sind grössere Mengen Na oder Fe nachteilig. Lässt man die Lösung durch ein H^+-Austauscherbett fliessen, so werden diese Nachteile beseitigt.[4,5] Interessant ist die "Auflösung" von $BaSO_4$[6] durch die Verschiebung des Lösungsgleichgewichtes mittels Kationenaustauscher. Der Sulfatgehalt kann volumetrisch, als freie Schwefelsäure ermittelt werden. Funasaka[7] bestimmt den Sulfatgehalt, indem er ihn in die Chloridform konvertiert, und potentiometrisch titriert. Gabrielson[8] bedient sich zur $PbSO_4$ Analyse mit H^+ Austauscher: die freie Schwefelsäure wird alkalimetrisch gemessen. In den erwähnten Methoden sind teils reine Sulfatlösungen nötig, die ohne weiteres gemessen werden können, teils sind Reinigungsoperationen erforderlich, die mühsam und zeitraubend sind, evtl. die Genauheit gefährden.

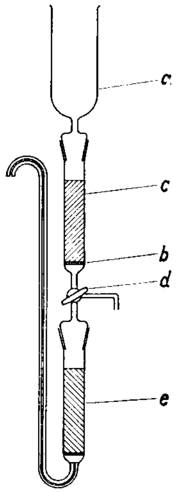

FIG. 1.

Unsere Arbeit über das physikalisch-chemische Verhalten unserer permselektiven Membranen[9] erforderte eine Vielzahl von $CuSO_4$-Bestimmungen, undzwar mit getrennter Sulfatanalyse. Wir suchten ein schnelles Routinverfahren, womit der SO_4-Gehalt neben Cu^{++} Ionen genau und einfach ermittelt werden kann.

Wir konvertieren die SO_4-Ionen an einem Anionenaustauscher stöchiometrisch in Chlorid und titrieren nach Mohr. In Spezialfällen, wenn die Lösung sauer anfällt, benützen wir die Volhardtsche Methode. Die störenden Kationen werden an einem Na^+-Austauscher zu Na^+ Ionen ausgetauscht, so sind die Umstände gleichgestellt. Enthält die Ausgangslösung auch Cl' Ionen, so muss dessen Gehalt vor dem Anionenaustausch mit einer Titrierung auch bestimmt, und dieser Wert vom Endresultat abgezogen werden. Evtl. vorliegender PO_4 Gehalt wird durch Magnesia-Mixture beseitigt. Der Niederschlag wird nicht filtriert: teils setzt er sich bei der Dekantierung ab, teils bleibt er über den Kationenaustauscher stecken und wird mit der Regeneriersäure abgewaschen.

Zur Ausführung der Bestimmungen entwickelten wir einen Apparat, in dem der ganze Prozess in einem Schritt vor sich geht (Abb. 1).

Die Behandlung des Apparates ist insofern einfach, dass mit einem Hahn die ganze Regulierung eingestellt wird, bloss die Lösungen werden eingeschüttet. Der Schwanenhals verhütet den Ablauf der Lösung vom Harz.[10] Die Methode gibt, mit kommensurablen Ionenverhältnissen in mässig verdünnten Lösungen eine Genauheit von rund ±1% rel. (Tab. I) Die Wiederbelebung geschieht mit Kochsalzlösung oder Salzsäure, die den Kationenaustauscher in die Na^+-bzw. H^+ Form, den Anionenaustauscher in die Cl' Form umwandeln, also in einem Schritt beide Harzbette regenerieren doch können mehrere Bestimmungen nacheinander ohne Regenerirerung durchgeführt werden (Tab. II).

TABELLE I

No.	Volum *ml*	Einwage $CuSO_4$ *mg*	Gemessen $CuSO_4$ *mg*	Titrierung 0,05*N* $AgNO_3$ *ml*	Fehler %
1	4	15,963	16,043	4,02	+0,5
2	4	15,963	15,833	3,97	−0,7
3	4	15,963	16,163	4,05	+1,2
4	4	15,963	16,043	4,02	+1,5
5	5	7,981	7,851	1,98	−1%
6	5	7,981	8,021	2,01	+0,5
7	5	7,981	7,981	2,00	0
8	5	7,981	8,061	2,02	+1,0

Das Harz wurde vor jeder Bestimmung regeneriert

TABELLE II

No.	Volum *ml*	Einwage $CuSO_4$ *mg*	Gemessen $CuSO_4$ *mg*	Titrierung 0,05*N* $AgNO_3$ *ml*	Fehler %
1	5	7,981	8,101	2,03	+1,5
2	5	7,981	7,851	1,98	−1
3	5	7,981	8,061	2,02	+1
4	5	7,981	7,981	2,00	0,0
5	5	7,981	8,021	2,01	+0,5

Die fünf Bestimmungen liefen ohne Zwischenregenerierung

EXPERIMENTELLER TEIL

Die Bestimmung verläuft wie folgt: Die zu analysierende Lösung, befreit von PO_4, CrO_4, WoO_4, MoO_4 od.dgl., wird im Normalkolben auf eine Konzentration von rund 0,01–0,05*N* verdünnt, einen evtl. Niederschlag (der doch kein SO_4'' enthalten darf) lässt man absetzen und aus der spiegelklaren Lösung messt man 2–6 ml (= 5–10 mg SO_4) in den Apparat (Abb. 1) für den Austauschvorgang ein.

Der Apparat ist in Na^+ bzw. Cl' Form, ionenfrei und mit demineralisiertem Wasser bis zum Schwanenhals gefüllt, zur Analyse bereit. Die obenerwähnte analysierende Lösung bringt man in den Vorraum (*a*), wobei der T-Hahn (*d*) geschlossen ist. Es wird darauf geachtet, dass die Lösung den Trichter (*a*) nur in dem erforderlichen Masse benetze, um leichte Nachspülmöglichkeit zu sichern.

Der Austausch verläuft mit einer Geschwindigkeit von rund 1 Tropfen/sec, also im abgebildeten Apparat (D = 7 mm, 1,5 ml. Harz) 2 ml in der Minute, = 5 cm/Min (3 m/h), bzw. 1,33 ml/ml/Min Durchsatz. Die Durchflüssgeschwindigkeit wird mit dem T-Hahn (*d*) reguliert, doch stellt sich das erwähnte Wert bei völliger Öffnung des Hahnes ein, falls die Kapillare 1 mm ϕ hat, die (*b*) Filterplatten aus G 1 Sinterglas und das Austauschmaterial aus einem Perlenpolymerisat von 0,1–0,2 mm ϕ bestehen.

Nachdem die Sulfatlösung durchgeflossen ist, wird der Apparat mit einmal 10 und einmal 5 ml ionenfreiem Wasser durchgespült und die gesamte Flüssigkeit mit 0,05 N $AgNO_3$ nach Mohr titriert.

Die gesamte Bestimmung verläuft in 20 Minuten.

Wenn die analysierende Probe auch Cl' Ionen entält, wird der Austauschprozess zweimal unternommen, einmal durch den Seitenweg (*d*), wobei darauf streng zu achten ist, das die Oberfläche der Flüssigkeit ständig über dem Harzschicht (*c*) bleibe, und einmal in der erwöhnten Weise, Beide gesammelten Flüssigkeiten unterliegen einer Mohr' schen Titrierung, wobei man mit der Differenz zu rechnen hat.

Materialien

Kationenaustauscher (*c*): *Mykion PS*, p.a., Polystyrolsulfonsäure Harzperlchen, 0,1–0,2 mm ϕ, Kapazität: 4,7 mAequ/g, 1,8 mAequ/ml (Farbstoff-Fabrik Füzfö, Ungarn).

Anionenaustauscher (*e*): *Mykion PA*, p.a., Polystyrolbenzyl-ammonium Harzperlchen, Typ II, 0,1–0,2 mm ϕ, Kapazität: 2,7 mAequ/g, 1,2 mAequ/ml (Farbstoff-Fabrik Füzfö, Ungarn).

Reagenzien: p.a. bzw. puriss. Präparate, der Firma Merck.

Wasser: Entionisiertes budapester Leitungswasser.

Beschickung des Apparates: Der mit Lauge und Säure durchgespülte Apparat, wird mit Wasser ausgewaschen und gefüllt. Die Harze werden in einem Becher mit Wasser aufgeschwämmt, 24 Stunden lang öfters mit neuem Wasser versetzt, dreimal mit Lauge und Säure (0,5.*N*–1.*N*) behandelt und in Na^+ bzw. Cl' Form so eingefüllt, dass die Behälter auch unter der Sinterplatten keine Luftblasen enthalten sollen. Danach erfolgt eine Regenerierung.

Forschungsinstitut für die Kunststoffindustrie,
Budapest, Hungary.

J. A. MIKES
J. SZANTÓ

LITERATUR

[1] A. Bahrdt, *Z. analyt. Chem.*, 1927, **70**, 109.
[2] M. Kehren und H. Stommel, *Chem. Ztg.*, 1927, **51**, 913; 1928, **52**, 163.
[3] E. Wiesenberger, *Mikrochem. Mikrochim. Acta*, 1942, **30**, 176.
[4] O. Samuelson *Z. analyt. Chem.*, 1939, **116**, 328.
[5] R. Kunin, *Amer. Soc. for Test. Mat.*, 1958. Symp. on Ion Exch., No. 195.
[6] G. H. Osborn, *Analyst*, 1953, **78**, 220.
[7] W. Funasaka und M. Kawane, *Chem. Abs.*, 1953, **47**, 12125e.
[8] G. Gabrielson und O. Samuleson, *Svensk Kem. Tid.*, 1950, **62**, 221.
[9] J. Mikes, J. Szánt6 und a., *Ung. Pat. Anm.* SE-865 (1958, nov. 10).
[10] J. Mikes, *Magyar Kém. Lap.*, 1956, **11**, 328.

Anhydrous magnesium perchlorate desiccant with added indicator

(*Received* 10 *August* 1959)

ANHYDROUS magnesium perchlorate as a new desiccant was first described by Willard and Smith[1] in 1922. The first application as desiccant was that of Smith, Brown and Ross.[2] Comprehensive studies of its preparation and properties were made by Smith and Rees,[3] Smith, Rees and Hardy[4] and Smith,[5] the latter study being that of its commercial application to the dehydration of air for use in liquefaction and fractionation to yield oxygen and nitrogen. The preparation of anhydrous magnesium perchlorate by dry reaction from ammonium perchlorate was described by Smith and Hardy.[6] Smith, Bernhart and Wiederkehr[7] made a study of its use in laboratory desiccator techniques.

Granular, porous, colourless magnesium perchlorate has been adopted almost universally for use in micro-combustion determination of hydrogen and carbon simultaneously. This desiccant is also employed in purging gases of ammonia. It is employed to determine ethyl alcohol in testing of drunken automobile operators[8] by the "intoximeter." Anhydrous granular and porous magnesium perchlorate is capable of dehydrating gases to a dew-point lower than that for liquid air temperatures[5] at high rates of flow contact, and with absorption capacity higher than any known desiccant. The same is true in its absorption of ammonia gas. It is commercially available under its chemical name and by the trade names "Anhydrone" and "Dehydrite".

An insistent demand has been made that anhydrous magnesium perchlorate be made commercially available with indicator properties added to give visual indication of complete capacity in the absorption of water. This communication describes the solution of this problem.

Potassium permanganate is isomorphous with magnesium perchlorate. When a saturated aqueous solution of magnesium perchlorate is allowed to crystallize by cooling from 110°–120° to room temperature, in the presence of 1–2% of potassium permanganate (based on the magnesium perchlorate content), the $Mg(ClO_4)_2{\cdot}6H_2O$ obtained is purple from co-crystallised permanganate.

Upon dehydration as previously described,[3,5] the anhydrous desiccant thus prepared is lighter purple in colour since dehydration at 200°–220°, with accompanying removal of water and developed porosity, produces a lighter hue. Upon absorption of water the spent reagent becomes dark brown.

This problem was solved particularly as an aid to the micro-analyst for use in filling Pregl tubes, wherein desiccant charges are small and demand indication of the extent to which reagent efficiency is at or near saturation, so as to lessen the frequency of recharging. Otherwise Pregl tube capacity may not be economically employed.

Department of Chemistry
University of Illinois, Urbana, Illinois, U.S.A.
G. FREDERICK SMITH

Department of Chemistry
Iowa State College, Ames, Iowa, U.S.A.
HARVEY DIEHL

REFERENCES

[1] H. H. Willard and G. Frederick Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2255.
[2] G. Frederick Smith, M. Brown and J. F. Ross, *Ind. Eng. Chem.*, 1924, **16**, 20.
[3] G. Frederick Smith and O. W. Rees, *ibid.*, 1931, **23**, 3513.
[4] G. Frederick Smith, O. W. Rees and V. R. Hardy, *J. Amer. Chem. Soc.*, 1932, **54**, 1328.
[5] G. Frederick Smith, *Chem. and Ind.*, 1934, 357.
[6] G. Frederick Smith and V. R. Hardy, *Z. anorg. Chem.*, 1935, **223**, 1.
[7] G. Frederick Smith, D. N. Bernhart and V. R. Wiederkehr, *Analyt. Chim. Acta*, 1952, **6**, 42.
[8] G. C. Forrester, *Chemical Tests for Alcohol in Traffic Law Enforcement.* Charles Thomas, pub., Springfield, Illinois.

Talanta, 1959, Vol. 3, p. 109. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEW

Advances in Inorganic Chemistry and Radiochemistry, Volume I. Edited by H. J. EMELEUS and A. G. SHARPE. Academic Press, Inc., New York, 1959. Pp. xi + 449. $12.00.

IN 1938 it was still possible for the senior editor of this book, in collaboration with J. S. Anderson, to present an essentially complete picture of the state of contemporary inorganic chemistry in a single volume of moderate size. The classic *Modern Aspects of Inorganic Chemistry* filled a gap in the literature, and, in its two editions, has for many years satisfied readers seeking a concise and readable account of the most active fields of inorganic chemistry. During the last ten years, however, the pace of new discovery in inorganic chemistry has accelerated enormously. It has become difficult to keep a book of this type reasonably up-to-date with new editions; while for one or two writers to prepare a really adequate and comprehensive new book on current developments would be a forbidding task. In the new circumstances, the best way of satisfying the hunger of chemists for up-to-date information on current work is to publish a continuing series of short, fully documented monographs by specialist contributors, a plan already successfully adopted in other branches of chemistry and physics. This first volume of *Advances in Inorganic Chemistry and Radiochemistry* contains nine chapters by leading research workers on subjects of strong current interest. It has not been unreasonably long in the press; there are many references from 1958 and one or two from 1959.

E. O. Fischer and H. P. Fritz's *Compounds of Aromatic Ring Systems and Metals* is perhaps the most welcome chapter in the book, other reviews of this subject being badly out-of-date. It includes a long section on benzene-metal compounds. The authors' viewpoint on bonding in the aromatic ring-metal compounds is refreshingly different from the Moffitt molecular orbital picture which has for long been rather uncritically accepted in the English language literature. W. N. Lipscombe on *Boron Hydrides* is mostly concerned with structure, especially three-centre bonds, and the topological theory of boron hydride structure. H. Taube's study of the *Mechanism of Redox Reactions* is an excellent piece of criticism in an extremely complex and difficult field. The chapter entitled *The Szilard–Chalmers Reaction in Solids* by G. Harbottle and N. Sutin demonstrates how this subject, not long ago a rag-bag of facts inexplicable except by guesswork, has developed a serious body of theory and shows signs of making useful contributions to our knowledge of solid-state chemistry and physics.

Analytical chemists will be most interested in the chapter by D. H. F. Atkins and A. A. Smales on *Activation Analysis*, which the writers describe as "a powerful addition to the armoury of modern analytical chemistry." They support this contention with a list of eighteen metals which can be detected in amounts of 10^{-9} gram or less by this method. The freedom of the activation method from reagent "blank" and contamination problems ensures that these high sensitivities can be used under practical conditions.

Phosphonitrilic Halides, by N. L. Paddock and H. T. Searle, deals with a group of compounds interesting both as inorganic polymers with possible technical applications, and as one of the starting points of the new inorganic chemistry of homologous series. The other contributions are *Lattice Energies* by T. C. Waddington, *Graphite Intercalation Compounds* by W. Rüdorff, and *The Sulphuric Acid Solvent System* by R. J. Gillespie and E. A. Robinson.

This book is too detailed and too fully documented to make easy reading for the non-specialist, but it and the subsequent volumes of the series will be essential works of reference for anyone whose main interest is in current inorganic chemistry, radiochemistry or analytical chemistry.

H. G. HEAL

Talanta, 1959, Vol. 3, p. 110. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged:

Tuesday 27 *October* 1959: **Society for Analytical Chemistry,** Midlands Section: *The Purity of Analytical Reagents:* Discussion will be opened by Mr. J. T. YARDLEY, B.Sc., F.R.I.C. Nottingham and District Technical College, Burton Street, Nottingham. 7.0 p.m.

Tuesday 27 *October* 1959: **Society for Analytical Chemistry,** North of England Section and Physical Methods Group: **Royal Institute of Chemistry,** North-East Coast Section: *Instrumental Developments in X-Ray Fluorescence Spectroscopy:* Mr. J. R. STANSFIELD, M.A., F. Inst. P. *Some Applications of X-Ray Spectrography:* Mr. H. I. SHALGOLSKY, B.Sc., A.R.I.C. Chemistry Lecture Theatre 2, King's College, Newcastle-upon-Tyne, 1. 6.30 p.m.

Friday 30 *October* 1959: **Society for Analytical Chemistry,** Scottish Section: *The Value of EDTA as an Analytical Reagent:* Dr. H. J. CLULEY, M.Sc., F.R.I.C. Chemistry Department, Queen's College, Dundee. 5.0 p.m.

Friday 30 *October* 1959: **Society for Analtyical Chemistry,** North of England Section: *The Changing Aspects of Chemical Analysis:* Mr. H. N. WILSON, F.R.I.C. Metropole Hotel, Stockton-on-Tees. 7.30 p.m.

Friday 30 *October* 1959: **Society for Anayltical Chemistry,** Western Section: **Royal Institute of Chemistry,** Mid-Southern Counties Section. *Analytical Chemistry and Clinical Diagnosis.* Professor Sir E. CHARLES DODDS, M.V.O., F.R.S. Salisbury.

Thursday 12 *November* 1950: **Society for Analytical Chemistry,** Midlands Section: *The Identification and Determination of Phenols:* Dr. L. BARKER. The University, Birmingham, 3. 6.30 p.m.

Friday 13 *November* 1959: **Society for Analytical Chemistry,** Scottish Section: **Royal Institute of Chemistry:** *Techniques in Radiochemistry for Analysis and Research:* Mr. D. A. LAMBIE, B.Sc., F.R.I.C. Royal College of Science and Technology, Glasgow. 7.15 p.m.

Tuesday 24 *November* 1959: **Society for Analytical Chemistry,** Physical Methods Group. Annual General Meeting. Burlington House, London, W.1. 6.30 p.m.

Saturday 5 *December* 1959: **Society for Analytical Chemistry,** North of England Section: *The Analysis of Cocoa and Chocolate in Relation to Modern Manufacturing Methods:* Mr. B. W. E. MINIFIE, F.R.I.C. and Mr. C. HARRIS, F.R.I.C. City Laboratories, Mount Pleasant, Liverpool. 2.15 p.m.

Wednesday 9 *December* 1959: **Society for Analytical Chemistry,** Midlands Section: *The Determination of Trace Impurities in Metals.* Discussion will be opened by Mr. B. BAGSHAWE, A. Met. and Mr. W. T. ELWELL, F.R.I.C. Wolverhampton and Staffordshire College of Technology, Wolverhampton. 7.0 p.m.

Wednesday 9 *December* 1959: **Society for Analytical Chemistry,** Biological Methods Group. Annual General Meeting. *Biological Methods in Forensic Science.* Dr. H. J. WALLS, B.Sc., Mr. S. S. KIND, B.Sc., and Dr. A. S. CURRY, M.A., A.R.I.C. Burlington House, London, W.1. 7.0 p.m.

Tuesday–Wednesday 3–4 *May* 1960: **Society for Analytical Chemistry: Iron and Steel Institute: Institute of Metals:** Joint Symposium on *Determination of Gases in Metals.* Church House, Westminster, London.

Three sessions are envisaged, occupying the afternoon of the 3rd and the morning and afternoon of the 4th. At the first session invited review papers will be presented covering the determinations of oxygen, hydrogen and nitrogen in a general way; the other two sessions will be devoted to shorter papers and discussions dealing with specialised aspects of the field.

It is intended that preprints of all the papers will be available before the start of the Symposium, and that the proceedings, including discussions, will be published in a single volume at a later date. Further information from the Hon. Secretary, Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1.

Talanta, 1959, Vol. 3, p. 111. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Activation Analysis of Trace Cobalt in Tissue using 10.5m-Cobalt. David G. Kaiser and W. Wayne Meinke. (7 *August* 1959).

Spectrophotometric Determination of Molybdenum in Steel with 3:3′:4′:5:7-pentahydroxyflavonone. Frank L. Chan and Ross W. Moshier. (30 *July* 1959).

The Preparation of Iridium Solutions by an Acid Attack of Tin-iridium Alloys. G. H. Faye and W. R. Inman. (30 *July* 1959).

Quantitative Oxidations by Potassium Ferricyanide: Bharat R. Sant and Suseela B. Sant. (7 *August* 1959).

The Precipitation of Zinc Sulphide from Acid Solutions by Thioacetamide. David F. Bowersox, Dwight M. Smith and Ernest H. Swift. (8 *August* 1959).

Potassium Bromate as Volumetric Reagent—I: Determination of Hydrazine and its Organic Derivatives. Balwant Singh and S. S. Sahota. (10 *August* 1959).

Titrimetric Analysis of 3:5-Dinitrobenzoate Derivatives. W. T. Robinson, R. H. Cundiff, A. J. Sensabaugh and P. C. Markunas. (10 *August* 1959).

Anhydrous Magnesium Perchlorate Desiccant with Added Indicator. G. Frederick Smith and Harvey Diehl. (10 *August* 1959).

The Colorimetric Determination of Boron in Nitrate Solutions. W. J. Ross and J. C. White. (10 *August* 1959).

Determination of Deuterium in Organic Compounds by Infrared Spectrophotometry R. Norman Jones and Marjory A. MacKenzie. (14 *August* 1959).

The Spectrophotometric Estimation of Phenol: With Special Reference to Solutions Containing Tyrosine, Tryptophane, Histidine or Chymotrypsin. W. Lee and J. H. Turnbull. (21 *August* 1959).

Solvent Extraction Separations of Platinum Metals—I: Ruthenium and Palladium. J. H. W. Forsythe, R. J. Magee and C. L. Wilson. (22 *August* 1959).

Solvent Extraction Separations of Platinum Metals—II: Rhodium, Palladium and Platinum. J. H. W. Forsythe, R. J. Magee and C. L. Wilson. (22 *August* 1959).

The Effect of Platinum Oxide Films on Reaction Kinetics at Platinum Electrodes. Donald G. Davis, Jr. (24 *August* 1959).

The Determination of Cobalt by Oxidation with Potassium Molybdicyanide. Byron Kratochvil and Harvey Diehl. (1 *September* 1959).

The Spectrophotometric Determination of Copper with Ammonium Pyrophosphate. C. J. Keattch. (2 *September* 1959).

New Redox Systems—I: Oxidation of Bivalent Cobalt with Iron^{III} Chloride in 1:10-Phenthroline solution F. Vydra and R. Přibil. (12 *September* 1959).

Oxidation-reduction Reactions on Ion-exchange Columns—I: Reduction of Iron^{III} Ions. L. Erdey, J. Inczédy and I. Markovits. (15 *September* 1959).

A New Micro Method of Studying the Thermal Stability of Easily Volatile Explosives. Vinzenz Anger. (21 *September* 1959).

A Critical Study of the Determination of Platinum with Dimethylphenylbenzylammonium chloride. A. D. Westland and L. Westland. (24 *September* 1959).

Titrimetric Determination of Soluble Silica as Silicomolybdic Acid. Takeo Takahashi and Shingo Miyake. (28 *September* 1959).

Talanta, 1959, Vol. 3, p. 112. Pergamon Press Ltd. Printed in Northern Ireland

BOOKS RECEIVED

Contributi Teorici e Sperimentali di Polarografia, Volume IV. Supplement to La Ricerca Scientifica, 1959. Centro di Polarografia, Via Loredan 4, Padova, Italy. Pp. 361.

The Analysis of Titanium and its Alloys, 3rd Edition. Imperial Chemical Industries Limited, 1959. Pp. 119. 21s.

The following publications have been received and are available from the Office of Technical Service, Department of Commerce, Washington 25, D.C., U.S.A.

An Automatic Recording Titrator. GERALD ROSS UMBREIT and J. S. FRITZ. LSC-1021. *December* 1957. Pp. iv + 50. $1.50.

The Determination of Plutonium in Irradiated Uranium Fuel Solutions by Controlled Potential Coulometry F. A. SCOTT and R. M. PEEKEMA. HW-58491. 10 *December* 1958. Pp. 29. $1.50.

Detection of Nitrite Ion in Plutonium Nitrate Solutions. M. O. FULDA. DP-336. *December* 1958. Pp. 7. $0.50.

An Analytical Method for Neptunium-237 Using Anion Exchange. F. P. ROBERTS. HW-59032. 28 *January* 1959. Pp. 15. $0.50.

Analysis for Neptunium by Controlled Potential Coulometry. R. W. STROMATT. HW-59447. 2 *February* 1959. Pp. 20. $0.75.

Spectrophotometric Study of the Ternary System, Aluminum Nitrate-Nitric Acid-Water: Application to Analysis. ROBERT W. HENRY and GLENN L. BOOMAN. IDO-14460. 31 *March* 1959. Pp. 11.

Remote Analytical Facility Operational Excercises. GEORGE A. HUFF. IDO-14434. 4 *April* 1959. Pp. 13. $0.50.

Extraction of Protoactinium with Diisobutylcarbinol. J. R. OLIVER, J. R. MERIWETHER and R. H. RAINEY. ORNL-2668. 15 *April* 1959. Pp. 13. $0.50.

An In-line Conductivity Meter with Temperature Compensation. D. W. COLVIN. DP-361. *April* 1959. Pp. 12. $0.50.

Van-Slyke Factors for Hydrogen, Oxygen, Carbon Dioxide and Carbon Monoxide. G. E. ADAMS and A. R. ANDERSON. ANL-5991. *April* 1959. Pp. 7.

Preparation of Lithium Isotope Standards—I: Separation of Sodium and Lithium by Dowex 50-X18 DVB Resin. W. C. DIETRICH and R. E. BARRINGER. Y-1254. 14 *May* 1959. Pp. 15. $0.50.

The Determination of Mercury, Copper and Zinc by Derivative Polarography—Application to Solutions of Uranyl Sulfate containing Corrosion Products. R. G. BALL, D. L. MANNING and O. MENIS. ORNL-2717. 25 *May* 1959. Pp. ii + 27. $1.00.

High Temperature Gas Chromatography of Aromatic Hydrocarbons: Instrument Design and Exploratory Studies at Temperatures up to 430°C. ROBERT A. BAXTER and ROBERT T. KEEN. NAA-SR-3154. 1 *June* 1959. Pp. 30. $1.00.

A New Apparatus for Liquid Phase Thermal Diffusion. EDWARD VAN HALLE. K-1420. 24 *June* 1959. Pp. x + 353. $5.00.

The Spectrographic Detection of Trace Impurities in Beryllium Oxide. O. P. KILLEEN. Y-1259. 4 *September* 1959. Pp. 12.

ERRATA

Vol. 2, *page* 226. *Legends to the Figs. should read as follows*:

Fig. 3. Continuous variations of the palladium complex with thiomalic acid.

Fig. 4. Slope ratio of the palladium complex with thiomalic acid. Curve (1), reagent in large excess; curve (2), palladium in large excess.

Note: The first slope in curve (2) is due to the formation of a 1 : 1 complex which absorbs less than the 2 : 1 complex. The second slope in curve (2) was used to establish the 2 : 1 ratio.

TALANTA

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(*Names of authors of books reviewed are in italics*)

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. Summaries will not be required for short or preliminary communications. For other contributions the essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. 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.

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5. 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.

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

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

[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.

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

[4] W. Jones, *Brit. Pat.* 654321, 1959.

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

7. Except in the case of preliminary communications, proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, when the amount of alteration makes it advisable.

8. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units.

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