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ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

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ELSEVIER PUBLISHING COMPANY
AMSTERDAM

✓ *Anal. Chim. Acta*, Vol. 29, No. 1, p. 1-96, July 1963

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Analytica Chimica Acta will have six issues to the volume, approx. 600 pages per volume, two volumes per year.

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 29, No. 1, July 1963

THE CONTINUOUS DETERMINATION OF LOW
CONCENTRATIONS OF CARBON DIOXIDE

(in French)

Low concentrations of carbon dioxide in gases can be determined by leading the gas over circulating water and measuring the conductivity.

The method can be extended to the determination of the carbonic acid content of water by means of another closed circuit of air, which is blown through the water sample.

Concentrations of the order of 0.0001% in inert gases and 1 p.p.b. in water can be determined with reasonable accuracy.

J. P. EHRENBURG ET G. B. SMIT, *Anal. Chim. Acta*, 29 (1963) 1-9

GRAVIMETRIC DETERMINATION OF COBALT AS PRESUMED
 $K_3Co(NO_2)_6$

The composition of 'potassium cobaltinitrite' precipitated under the usual conditions from a slightly acid solution containing a large excess of potassium nitrite, and finally dried at 110°, has been determined. When a relatively small quantity of cobalt is precipitated the dried precipitate consists of a mixture of anhydrous and hydrated $K_3Co(NO_2)_6$. With large amounts of cobalt the precipitate also contains a salt of cobalt(II) (probably $K_3Co(NO_2)_4$) due to incomplete oxidation of the cobalt(II). Because the formula weight of $K_3Co(NO_2)_4$ is smaller than that of $K_3Co(NO_2)_6$, whereas that of hydrated $K_3Co(NO_2)_6$ is larger, the weight of the precipitate is actually not very different than if it were pure $K_3Co(NO_2)_6$. Quantities of cobalt from 40 to 300 mg can be determined with an error within $\pm 1\%$ by weighing the dried precipitate as presumed $K_3Co(NO_2)_6$, and, if desired, the error can be decreased to a few tenths of a percent by employing an empirical factor. This simple method rivals in accuracy the more laborious electrogravimetric method.

J. J. LINGANE, P. J. LINGANE AND M. D. MORRIS, *Anal. Chim. Acta*,
29 (1963) 10-21

DETERMINATION OF TRACES OF FREE ACID IN URANYL
SALT SOLUTIONS

A method for the determination of free acid in the presence of uranium(VI) is suggested. It involves the extraction of uranium by TBP from a solution saturated with potassium nitrate or chloride in order to prevent interference from the hydrolysis of uranium. The end-point is detected potentiometrically at pH 3.4. The method is suitable for the determination of 0.1-1.5 millimoles of acid in the presence of as much as 1.0 millimole of uranium.

J. MASHALL AND A. BAR-NUN, *Anal. Chim. Acta*, 29 (1963) 22-26

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM WITH 8-MERCAPTOQUINOLINE

8-Mercaptoquinoline was found to be sensitive for the colorimetric determination of molybdenum. A procedure is outlined in which the complex formed, $\text{Mo}(\text{C}_9\text{H}_6\text{NS})_2$, is extracted into chloroform and the extinction measured at $425 \text{ m}\mu$. The effects and removal of interfering ions are discussed.

R. J. MAGEE AND A. S. WITWIT, *Anal. Chim. Acta*, 29 (1963) 27-30

STUDIES ON URONIC ACID MATERIALS

PART VIII. A COMPARATIVE STUDY OF SOME COLORIMETRIC METHODS OF ESTIMATING THE URONIC ACID CONTENT OF POLYSACCHARIDES

Values for the uronic acid content of a variety of polysaccharide materials were obtained by colorimetric methods and by acidic decarboxylation; very large differences were found, particularly for heterogeneous biological materials. Colorimetric methods are useful for "screening" many samples rapidly, and for routine or comparative measurements on characterised products. For materials of unknown structure, however, colorimetric results should be interpreted with caution, especially when shortage of material does not permit corroborative decarboxylation or titration values to be obtained.

D. M. W. ANDERSON AND S. GARBUTT, *Anal. Chim. Acta*, 29 (1963)
31-38

STUDIES ON URONIC ACID MATERIALS

PART IX. THE SIMULTANEOUS DETERMINATION OF URONIC ACID AND ALKOXYL GROUPS IN POLYSACCHARIDES BY REFLUX WITH HYDRIODIC ACID

A reaction period of 2.5 h is required for the decarboxylation of uronic groups with 19% (w/w) hydrochloric acid, but 55% (w/w) hydriodic acid gives complete decarboxylation in 1.5 h. This rapid reaction can be carried out in a standard Zeisel reaction flask and condenser. Vapour phase infra-red spectroscopy gives a specific determination of the carbon dioxide evolved, and facilitates simultaneous determinations of any alkoxy groups present. The proposed method is particularly useful for pectins and plant gums; it gives greater sensitivity and reproducibility than previous methods.

D. M. W. ANDERSON, S. GARBUTT AND S. S. H. ZAIDI, *Anal. Chim. Acta*, 29 (1963) 39-45

KINETICS OF THE EXTRACTION OF CHROMIUM(III) INTO CHLOROFORM CONTAINING ACETYLACETONE

The extraction of chromium(III) from perchlorate and chloride media into chloroform containing acetylacetonone has been investigated from the kinetic viewpoint. The effects of pH, reagent concentrations, and several other variables are reported.

H. E. HELLEWEGE AND G. K. SCHWEITZER, *Anal. Chim. Acta*, 29
(1963) 46-51

THE DETERMINATION OF TITANIUM IN METEORITIC MATERIAL

A method utilizing tiron for the determination of titanium in meteorites is described. Iron interference is avoided by formation of the ferric-EDTA complex at low pH, followed by reduction to the ferrous-EDTA complex at pH 5.6. Results for actual meteorite solutions agreed well with those obtained by the hydrogen peroxide method, thus the advantages of the greater sensitivity of tiron may be gained without loss of accuracy.

A. J. EASTON AND L. GREENLAND, *Anal. Chim. Acta*, 29 (1963) 52-55

STUDIES ON THE SOLVENT EXTRACTION OF YTTRIUM THENOYLTRIFLUOROACETONATE

Studies of extractions of yttrium from aqueous solution into chloroform, benzene, methyl isobutyl ketone, and mixtures of these solvents, containing thenoyltrifluoroacetone are described. The effects of reagent concentration, added *n*-butylamine, and added fluoride were investigated. Values of $pH_{1/2}$ and P_e were determined, and identifications of the involved species are suggested.

G. K. SCHWEITZER AND S. W. McCARTY, *Anal. Chim. Acta*, 29 (1963)
56-60

POLAROGRAPHIC DETERMINATION OF INDIUM IN LEAD AND ZINC METALS

A rapid polarographic method for determining low milligram quantities of indium in lead metal containing 2% of zinc and in zinc metal containing 2% of lead is described. In a supporting electrolyte of 10% D-tartaric acid adjusted to pH 2.0, a well-defined wave for indium is obtained after the precipitation of lead as the sulfate.

R. J. HOFER, R. Z. BACHMAN AND CH. V. BANKS, *Anal. Chim. Acta*,
29 (1963) 61-65

THERMOGRAVIMETRIC STUDY OF LANTHANUM, PRASEODYMIUM AND NEODYMIUM PICOLINATES AND DIPICOLINATES

(*Short Communication, in French*)

LAURENT MOYNE ET GERMAINE THOMAS, *Anal. Chim. Acta*,
29 (1963) 66-69

A MODIFIED METHOD FOR THE TITRIMETRIC DETERMINATION OF MANGANESE IN ORES AND METALS

(*Short Communication*)

J. DOLEŽAL, J. ZÝKA AND G. DONOSO, *Anal. Chim. Acta*, 29 (1963)
70-73

ANALYTICAL POSSIBILITIES OF A SERIES OF NEW AROMATIC-TYPE CHELATE COMPOUNDS

(*Short Communicaton*)

A. J. CAMERON, N. A. GIBSON AND R. ROPER, *Anal. Chim. Acta*, 29
(1963) 73-75

DETERMINATION OF SOME ORGANIC HALIDES BY FORMATION OF BUNTE SALTS WITH THIOSULPHATE AND IODIMETRY

(Short Communication)

M. R. F. ASHWORTH AND M. WINTER, *Anal. Chim. Acta*, 29 (1963) 75-78

INFRARED SPECTROPHOTOMETRY OF AQUEOUS NITRATE, NITRITE AND SULFATE SOLUTIONS

(Short Communication)

A. L. UNDERWOOD, MICHAEL W. MILLER AND LYMAN H. HOWE, III
Anal. Chim. Acta, 29 (1963) 79-81

DETERMINATION OF TRACES OF COPPER

(Short Communication)

L. DE ROO, J. F. M. TERTOOLEN AND C. BUIJZE, *Anal. Chim. Acta*, 29 (1963) 82

TITRIMETRIC DETERMINATION OF IRON(III) WITH TITANIUM(III) AT ROOM TEMPERATURE

(Short Communication)

P. V. KRISHNA RAO AND G. GOPALA RAO, *Anal. Chim. Acta*, 29 (1963) 82-84

COMPLEX FORMATION AND FLUORESCENCE
PART III. SALICYLATE COMPLEXES

(Short Communication)

J. A. BISHOP, *Anal. Chim. Acta*, 29 (1963) 84-87

A SENSITIVE METHOD FOR END-POINT DETECTION
IN CONSTANT CURRENT COULOMETRY

(Short Communication)

K. F. LAUER AND Y. LE DUIGOU, *Anal. Chim. Acta*, 29 (1963) 87-89

A NEW MICROSCOPIC CRYSTAL TEST FOR BERYLLIUM
WITH HEXAMMINOCOBALT(III) CHLORIDE

(Short Communication)

J. W. L. VAN LIGTEN AND W. COOL, *Anal. Chim. Acta*, 29 (1963) 89-92

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AMSTERDAM

Anal. Chim. Acta, Vol. 29 (1963)

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NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

MÉTHODE CONTINUE POUR LE DOSAGE DE L'ACIDE CARBONIQUE
EN FAIBLES CONCENTRATIONS

J. P. EHRENBURG ET G. B. SMIT

*Laboratoires de la N.V. tot Keuring van Electrotechnische Materialen,
Arnhem (The Netherlands)*

(Reçu le 15 novembre, 1962)

INTRODUCTION

Le dosage de faibles concentrations de dioxyde de carbone dans l'eau, par exemple, permet de déterminer l'efficacité d'un dégazeur atmosphérique dans une installation de déminéralisation.

Dans ce but, nous avons établi une méthode avec enregistrement permettant d'examiner des eaux ayant une teneur en CO_2 de l'ordre du microgramme par litre.

Contrairement aux méthodes en usage en physiologie, où l'on ne dispose en général que de petites quantités d'échantillon, il s'agit dans notre cas de doser des faibles teneurs, en ayant à sa disposition des quantités considérables d'échantillon.

Dans la plupart des méthodes applicables, on chasse le dioxyde de carbone de l'échantillon et on le dose après absorption: soit dans une solution de $\text{Ba}(\text{OH})_2$ dont on mesure l'excès¹ ou la diminution de conductivité², soit dans une solution de BaCl_2 avec titrage coulométrique³, soit dans la pyridine (titrage à l'acétate)⁴. La méthode par dérivation des valeurs p et m de l'eau⁵ s'est montrée moins appropriée, surtout aux faibles concentrations⁶.

Nous avons développé une méthode selon laquelle on fait équilibrer un circuit d'air avec l'eau à examiner. Cet air, qui, à son tour, alimente un circuit d'eau pure de CO_2 jusqu'à l'équilibre. Dans ce second circuit, la conductivité est mesurée ou enregistrée. Pour déterminer la teneur en CO_2 total, on acidifie l'eau à analyser.

La seconde partie de l'appareil permet de déterminer la teneur en dioxyde de carbone des gaz indifférents, mis directement en contact avec le circuit d'eau.

DÉVELOPPEMENT DE L'APPAREIL

Il est bien connu que l'absorption du dioxyde de carbone ne se fait pas instantanément, même dans des solutions plus ou moins alcalines.

Dans le cadre d'un symposium sur l'absorption de gaz dans des liquides⁷, LEWIS ET WHITMAN ont traité ce problème, d'une manière générale pour des gaz quelconques. Ils admettent à la surface de contact un film gazeux et un film liquide, dans lesquels ils localisent une résistance de passage du gaz. Leurs considérations sont toujours valables. Les déductions de KISHINEVSKII ET MOCHALOVA⁸ nous semblent également importantes; ils introduisent un coefficient pour la diffusion turbulente. NIJSING, HENDRIKSZ ET KRAMERS⁹, de leur côté, considèrent le film liquide et le reste du liquide comme un ensemble; ceci nous semble plus réel. Cependant, l'étude de ces

derniers auteurs se base sur un film glissant tellement vite le long d'une paroi, que le CO_2 n'a pas le temps d'atteindre la surface de contact entre l'eau et la paroi de support. D'autre part, en regardant la saturation d'un film relativement mince, les considérations de LEWIS ET WHITMAN nous ont fourni les données nécessaires.

Ils admettent à la surface de contact un film de gaz et un film de liquide, dans lesquels les conditions diffèrent de celles des phases gazeuse et liquide en général: en cas de transport de gaz de la phase gazeuse à la phase liquide, la pression partielle du gaz dans le film diminue, de la pression dans la phase gazeuse à la pression à la surface de contact; de plus, la concentration du gaz dans le film liquide diminue de la concentration à la surface de contact à la concentration dans le liquide. La pression et la concentration à la surface de contact obéissent à la loi de Henry. Ces considérations conduisent à la relation suivante, exprimant l'égalité des transports de gaz à travers les films gazeux et liquide:

$$dW/Ad\theta = k_g(P_g - P_l) = k_l(C_l - C_i)$$

$dW/d\theta$ = vitesse de transport du gaz

A = étendue de la surface de contact

k_g = coefficient de diffusion à travers le film gazeux

P_g = pression partielle du gaz dans le film gazeux, par rapport à la phase gazeuse

P_l = pression partielle du gaz dans le film gazeux, au côté de la surface de contact

k_l = coefficient de diffusion à travers le film liquide

C_l = concentration du gaz dans le film liquide, au côté de la surface de contact

C_i = concentration du gaz dans le film liquide, au côté de la phase liquide.

Le transport total du gaz est exprimé par:

$$dW/Ad\theta = K_g(P_g - P_l) = K_l(C_g - C_l)$$

où P_l est la pression partielle du gaz en équilibre avec C_l , et C_g la concentration en équilibre avec P_g ; K_g et K_l sont alors les coefficients de diffusion pour les deux films ensemble, K_g étant exprimé dans les dimensions de gaz (atm) et K_l dans les dimensions de liquide (g/cm^3). Dans le cas des gaz très solubles, on peut négliger le film liquide; le film gazeux détermine le transport entre les phases. Dans le cas des gaz peu solubles, le film gazeux perd son importance. Pour des gaz de solubilité moyenne, il faut considérer l'un et l'autre et selon les circonstances c'est la résistance du film gazeux ou celle du film liquide qui domine.

Dans l'appareillage considéré, nous avons deux surfaces de contact: eau/air et air/eau. Avec un accroissement de la teneur en CO_2 de l'eau à examiner, un peu de CO_2 passe dans l'air et de là dans l'eau circulante, jusqu'à ce que le nouvel équilibre soit atteint. L'appareil doit être construit de manière telle que le temps nécessaire à atteindre le nouvel équilibre soit limité. On considère la surface de contact eau/air et on suppose qu'au commencement l'air est en équilibre avec l'eau à examiner; le CO_2 contenu dans l'air a une pression partielle de P_g . Il faut se demander maintenant comment on pourra limiter le temps pour que la différence $P_g - P_l$ tombe, par exemple, à une valeur de 0.01 ($P_g - P_l$) en abaissant la concentration dans l'eau à une valeur qui est en équilibre avec une pression partielle P_l . Pour ce temps, une expression peut être dérivée de l'équation donnée par LEWIS ET WHITMAN, à savoir:

$$dW/Ad\theta = k_g(P_g - P_l)$$

en tenant compte du fait que la quantité W grammes de gaz causant la diminution $P_g - P_l$ de la pression du CO₂ dans l'air, varie linéairement avec le volume V de l'air:

$$W = VH(P_g - P_l)$$

Dans cette équation le terme H sert à égaliser les dimensions des deux membres, terme que l'on retrouve également dans l'équation de la loi de Henry. L'expression

$$dW = VHd(P_g - P_l)$$

peut être introduite dans l'équation de LEWIS-WHITMAN; d'où

$$d\theta = \frac{VH}{AK_g} \cdot \frac{d(P_g - P_l)}{P_g - P_l}$$

$$\theta = \frac{VH}{AK_g} \cdot \ln \frac{(P_g - P_l)_1}{(P_g - P_l)_2}$$

Pour réduire $P_g - P_l$ par exemple à un centième de sa valeur initiale, il faut le temps

$$\theta_{0.01} = 4.6 \frac{VH}{AK_g}$$

Cette expression montre qu'il faut avoir des surfaces de contact aussi grandes que possible, en raison du volume de la phase qui doit absorber ou libérer le CO₂, car V sera limité.

Les concentrations de CO₂ dans l'eau et dans l'air, se trouvant en équilibre à 20°, toutes deux exprimées par exemple en mg/l, sont du même ordre (à cette température 1 mg CO₂/ml de gaz est en équilibre avec 0.934 mg CO₂/ml d'eau); cela signifie que:

(1) le volume d'air circulant sera beaucoup moins élevé que le volume de l'eau à examiner, qui passe dans le temps choisi comme limite de réponse de l'appareil à un changement de la concentration (*p.e.* $\theta_{0.01}$ de la formule);

(2) au point de contact, où l'eau à examiner doit s'équilibrer avec l'air, on prendra soin d'un arrangement tel que la quantité de CO₂ qui doit passer de l'eau dans l'air pour établir l'équilibre, n'affaiblisse que relativement peu la concentration du CO₂ de l'eau.

Et par conséquent:

(3) le volume d'eau circulant dont on a mesuré la conductivité sera moins important que le volume de l'air circulant;

(4) au deuxième point de contact, où l'air circulant doit s'équilibrer avec l'eau circulante, le passage du CO₂ de l'air dans le circuit d'eau n'attaquera que peu le niveau de la concentration du CO₂ de l'air circulant.

Au regard de (2), nous avons placé comme premier point de contact, où l'eau à examiner et l'air circulant doivent s'équilibrer, un filtre de verre fritté à travers lequel l'air est soufflé en fines bulles dans l'eau, conduite par un tube vertical, circulant en contre-courant par rapport aux bulles d'air.

De plus ce dispositif a l'avantage de tenir compte du fait, indiqué par LEWIS ET WHITMAN *e.a.*, que la résistance de passage du CO₂ est due en particulier au film liquide bordant la surface de contact; car, lavant l'eau à examiner des petites bulles d'air, ce film se rafraîchit toujours. En choisissant une combinaison appropriée entre

la finesse du filtre de verre, le diamètre du tube et le débit d'alimentation le contre courant peut réaliser l'équilibre exact entre l'eau entrant et l'air sortant, même lors d'une alimentation de peu de litres par heure.

Quant à (4) nous avons conçu un flacon vertical de verre, d'une forme telle que l'eau du second circuit entre au-dessus et coule également par-dessus la paroi intérieure du récipient, formant un film le long duquel circule en contre-courant l'air qui passe aussi le premier filtre.

Pour ce film, le calcul donné pour le premier filtre est également valable; cependant, il faut remarquer que pour le film, il ne s'agit pas d'un volume V total de l'eau circulante, mais de l'équilibre de l'eau courante sur la paroi.

En supposant que la résistance à l'absorption est située entièrement dans le film

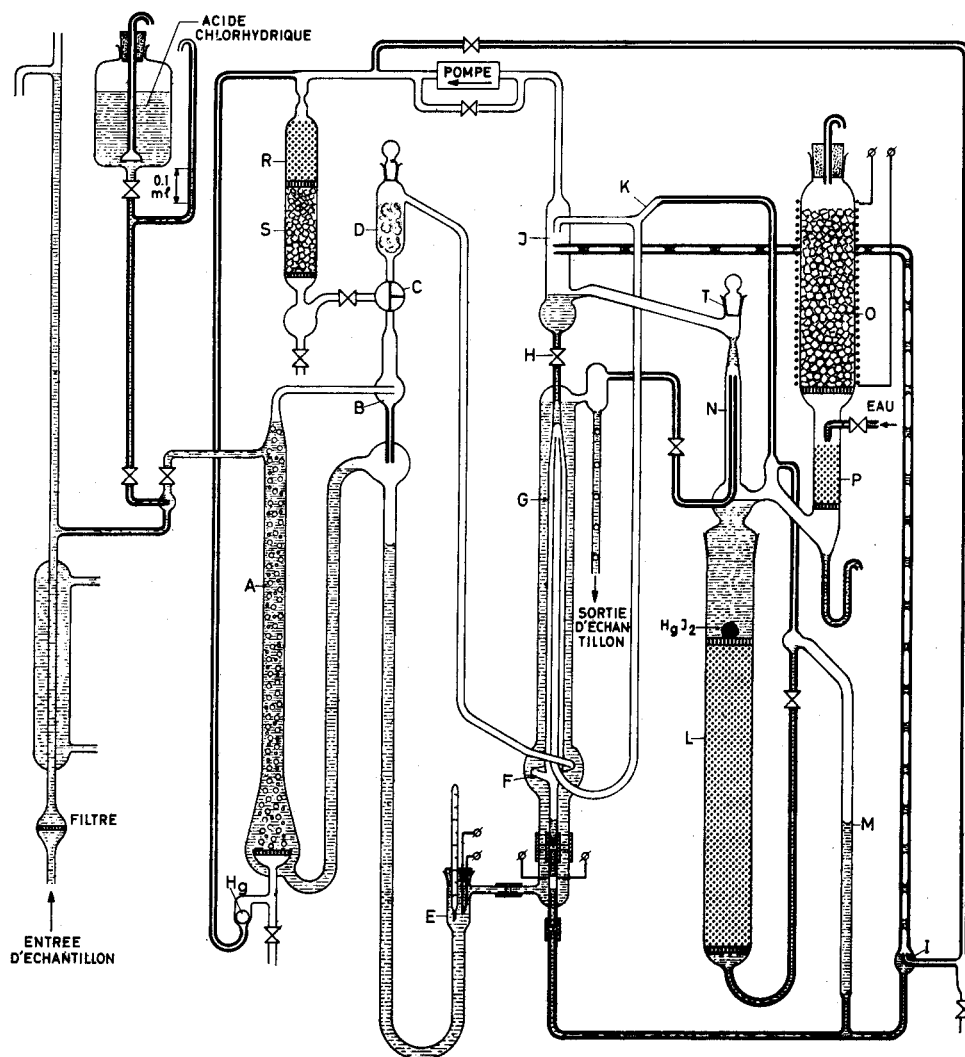


Fig. 1. Appareil pour la détermination de faibles concentrations d'acide carbonique.

liquide à la surface de contact et par conséquent qu'il n'y a pas un gradient de concentration dans le reste du film passant sur la paroi, on a pour chaque élément du film avec surface dA :

$$\theta_{0.01} = \frac{4.6H}{K_g} \cdot \frac{dV}{dA} = \frac{4.6H}{K_g} \cdot \delta,$$

équation dans laquelle δ est l'épaisseur du film et K_g/H est (selon HASLAM *et al.*¹⁰) 36.5 cm/h.

En exigeant qu'en bas du cylindre, l'équilibre soit approximé jusqu'à 1%, on peut écrire pour le débit Q de l'eau

$$Q\theta_{0.01} = ph\delta$$

Dans cette équation h est la hauteur et p la circonférence du cylindre. En éliminant $\theta_{0.01}$ et en combinant les facteurs qui sont constants, on obtient :

$$h = C \cdot Q/p$$

Dans notre appareil nous avons choisi $Q/p = 0.01$ cm²/sec et par conséquent pour h 4-6 cm au moins. Pour être sûr, nous avons augmenté cette valeur jusqu'à 25 cm.

Nous avons vérifié l'efficacité du récipient échangeur en introduisant de l'eau saturée de dioxyde de carbone et de l'air exempt de CO₂; nous avons constaté que la teneur en CO₂ de l'eau à la sortie était abaissée à une fraction de <0.1% de sa valeur initiale.

Un schéma de l'appareil est donné (voir Fig. 1).

Il faut mentionner qu'au moyen de la seconde partie de cet appareil, il est possible de déterminer de manière continue et d'enregistrer de faibles teneurs de CO₂ dans des gaz; cependant, il faut prendre soin d'en éloigner les autres composés volatils, formant des ions dans l'eau.

DESCRIPTION DE L'APPAREIL

D'après la Fig. 1, on voit que l'eau à examiner est conduite à travers A par un disque filtrant de verre fritté (G₃) qui assure un bon contact avec l'air injecté. A ce récipient est ajouté un dispositif B évitant l'entraînement de gouttelettes par le courant d'air. L'eau est acidifiée par de l'acide chlorhydrique 1 : 10,000. L'eau passe au préalable sur un manchon pour que la température au second point de contact air/eau soit égale à celle du premier. Cette température est mesurée en E, où on peut aussi appliquer la compensation de température corrigeant un système enregistreur.

L'air, poussé continuellement par une pompe de capacité adaptée (d'au moins 100 ml/min et réglée par un court-circuit) sans fuites, fait passer l'eau à examiner en A et à travers un filtre D de laine de quartz afin d'éliminer les dernières gouttelettes d'eau; après une acclimatation dans la petite spirale F, elle passe à travers le film du second circuit d'eau produit au côté intérieur de la paroi de G en ajustant le robinet régulateur H, qui ne doit pas être graissé. L'air passe à l'intérieur de G et retourne à la pompe. Le niveau de la pression de l'air circulante est fixé par une connection à l'air ambiant via K.

L'eau du second circuit, après avoir passé per G, comme film à la paroi, se rassemble au fond et passe à travers la cellule de mesure de conductivité. Elle est ensuite

conduite à travers un tube capillaire, donnant une résistance adaptée au point I, où un embranchement réglable du côté poussant de la pompe effectue l'ascension au récipier séparateur J.

Pour un fonctionnement de G, il faut que le film couvre toute la paroi, ce qui exige:

- (1) une position exactement verticale et une forme coulante sans inégalités de G;
- (2) un dégraissage minutieux de l'appareil;
- (3) une absence de vapeurs grasses en évitant des surfaces exposées de caoutchouc et de bakelite, etc. et en utilisant des serpentins de polythène (pas de PVC);
- (4) pour des teneurs pas trop faibles de CO_2 on peut diminuer l'influence de graisse en ajoutant une faible quantité de détergent non-ionogène;
- (5) une injection de l'eau à la mise en marche de l'appareil en ouvrant complètement H pour quelques instants; c'est pour cela qu'il faut un petit réservoir, directement au-dessus de H.

Cettes mesures permettent une humidification permanente de G sans détergent et sans dégraisseur.

En outre, l'eau du second circuit peut être contaminée par des ions provenant du verre de l'appareil, donnant une conductivité qui s'additionne celle de l'acide carbonique. Cette contamination est évitée en utilisant du verre Pyrex, en couvrant toutes les surfaces suspectes d'une mince couche de matériaux inertes, et en conduisant une partie de l'eau circulante à travers une colonne L d'échangeur d'ions "mixed bed", qui doit être dégraissée de même. La fraction qu'on laisse passer sur l'échangeur est adaptée à la concentration à déterminer et monte de 0.1 pour 100 μg et plus par litre jusqu'à 0.5 pour l'ordre de 1 $\mu\text{g/l}$; le débit peut être contrôlé en observant le niveau M.

A l'exception de faibles teneurs, il est utile de protéger le "mixed bed" contre un épuisement prématuré par le CO_2 , au moyen d'un petit dégazeur N, à travers lequel est aspiré un peu d'air purifié par de la chaux sodique dans O (1 l/h suffit). Pour éviter que cet air assez sec cause une perte continue d'eau du second circuit d'eau, on le chauffe en O par 2 watts par exemple, de sorte que de l'eau introduite en P (avec s'échangeur d'anions) à raison d'une goutte par heure, s'évapore et s'ajoute au circuit.

Le remplissage initial du second circuit d'eau est effectué via T.

Enfin il est avantageux de faire un essai à blanc en remplaçant A (+B) par une section R/S, où les vapeurs acides ou alcalines sont absorbées dans l'échangeur de cations et la chaux sodique, dégraissée par chauffage.

Nous avons obtenu pour l'essai à blanc une conductivité ne dépassant que faiblement celle de l'eau absolue.

RÉSULTATS

Avec l'appareil décrit, nous avons examiné des solutions de Na_2CO_3 de concentrations différentes.

Pour vérifier les valeurs obtenues nous avons essayé de calculer les conductivités qui devraient être trouvées. Ceci est possible en considérant que selon la loi de Henry le CO_2 gazeux n'est en équilibre qu'avec le CO_2 dissous moléculaire. Or, le CO_2 moléculaire du second circuit, qui n'est pas acidifié, est égal au CO_2 total de l'eau examinée, si cette dernière contient un acide diminuant la dissociation de l'acide carbonique.

Partant de:

$$k = [H^+][HCO_3^-]/[CO_2]$$

$$[H^+] = [HCO_3^-] + [OH^-]$$

$$\kappa = l_{H^+}[H^+] + l_{OH^-}[OH^-] + l_{HCO_3^-}[HCO_3^-]$$

on peut déduire:

$$\kappa = (l_{H^+} + l_{HCO_3^-})[H^+] + (l_{OH^-} - l_{HCO_3^-}) k_w/[H^+]$$

où

$$[H^+] = \sqrt{k \cdot [CO_2] + k_w}$$

Dans ces équations:

k = constante de l'acide carbonique

κ = conductivité

l = vitesse des ions

pour lesquels nous avons les valeurs

	20°	25°	30°
$k \cdot 10^7$	4.04	4.31	4.54
$k_w \cdot 10^{14}$	0.681	1.008	1.471
l_{H^+}	325	350	375
l_{OH^-}	182	200	218
$l_{HCO_3^-}$	40	445	50

Nous avons mesuré des concentrations de 1, 2, 5, 10, 20, 50, 100, 200, 500 µg et 1, 2, 5, 10 et 20 mg CO₂/l aux températures 20, 25 et 30°.

Nous avons soustrait des conductivités trouvées la différence de celle de l'essai à blanc et la conductivité théorique de l'eau, pour laquelle nous avons utilisé respectivement 0.0419, 0.0552 et 0.0722 µS/cm.

TABLEAU I
CONDUCTIVITÉS DES SOLUTIONS D'ACIDE CARBONIQUE EN µS/cm

κ ₂₀	κ ₂₅	κ ₃₀	c _{CO₂}	
			Introduit	Mesuré
0.0537	0.0667	0.0827	1	1.1 µg/l
0.0639	0.0770	0.0934	2	2.25 µg/l
0.0878	0.1022	0.1189	5	4.95 µg/l
0.1176	0.1344	0.1534	10	9.8 µg/l
0.1613	0.1824	0.2050	20	19.2 µg/l
0.2503	0.2807	0.3129	50	51.8 µg/l
0.3515	0.3935	0.4367	100	99.1 µg/l
0.4957	0.5535	0.613	200	198 µg/l
0.7820	0.8725	0.966	500	495 µg/l
1.105	1.233	1.365	1	1.005 mg/l
1.563	1.743	1.932	2	2.00 mg/l
2.473	2.760	3.057	5	5.02 mg/l
3.490	3.893	4.312	10	10.1 mg/l
4.490	5.512	6.105	20	20.15 mg/l

Les mesures à 25 et 30° sont des mesures préliminaires aux concentrations plus élevées, dont le coefficient de température mesuré concorde avec celui qu'on peut dériver des conductivités, calculées pour 20, 25 et 30°, en tirant les constantes à ces températures; on peut écrire pour des concentrations > 200 µg/l:

$$k_t = \kappa_{20}\{1 + 0.0228(t - 20) + 0.00008(t - 20)^2\}$$

Nous avons enfin établi une série de mesures exactes, à toutes les concentrations indiquées, à 20°.

Les résultats sont donnés dans le Tableau I, où la conductivité est exprimée en µS/cm. Le Tableau contient aussi les valeurs de la conductivité calculée pour 25 et 30°. La détermination s'effectuera souvent à des températures un peu plus élevées.

Nous avons repris les valeurs pour 20 et 30° dans la Fig. 2.

La méthode décrite permet donc de doser, en quelques minutes, de faibles teneurs en CO₂ d'eaux dégazées, avec une grande sensibilité et une précision suffisante.

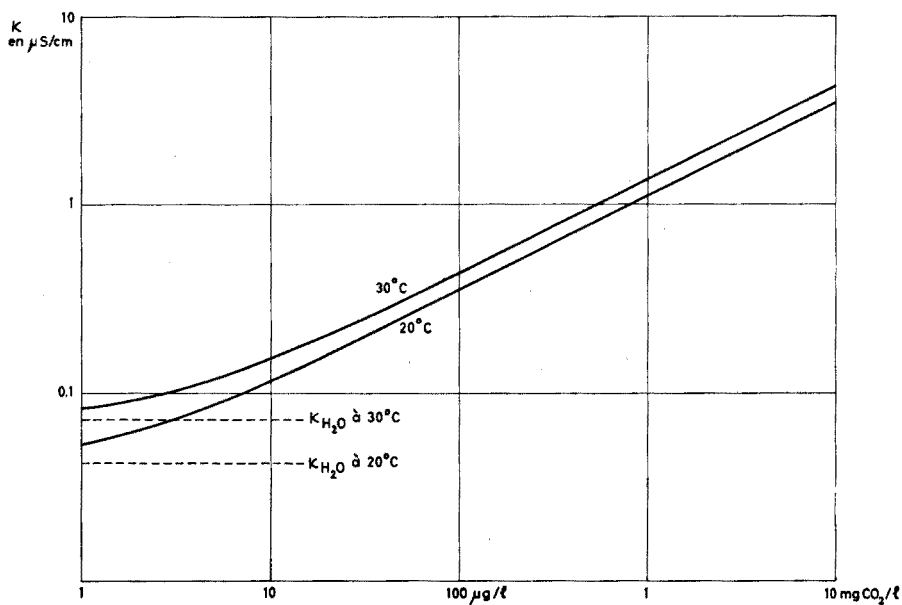


Fig. 2. Conductivités des solutions d'acide carbonique à 20° et 30°.

RÉSUMÉ

De faibles concentrations de dioxyde de carbone dans des gaz peuvent être déterminées par passage du gaz dans de l'eau en circulation et mesure de la conductivité de cette eau.

La méthode peut être appliquée au dosage de l'acide carbonique dans l'eau, en formant un autre circuit fermé d'air, qui passe également à travers un courant de l'eau à examiner.

On peut déterminer ainsi des concentrations de l'ordre de 0.0001% dans des gaz indifférents et de 1 µg/l dans l'eau, avec une précision suffisante.

SUMMARY

Low concentrations of carbon dioxide in gases can be determined by leading the gas over circulating water and measuring the conductivity.

The method can be extended to the determination of the carbonic acid content of water by means of another closed circuit, of air, which is blown through the water sample.

Concentrations of the order of 0.0001% in inert gases and 1 p.p.b. in water can be determined with reasonable accuracy.

ZUSAMMENFASSUNG

Kleine Mengen von Kohlendioxyd in Gasen können dadurch bestimmt werden, dass man das Gas über zirkulierendes kontinuierlich Wasser strömen lässt und dessen Leitfähigkeit misst.

Die Methode trifft auch zu zur Bestimmung des Kohlensäuregehaltes von Wasser, wenn der Gasstrom, gleichfalls zu einem geschlossenen zirkulierenden System gemacht, seinerseits durch einen Strom des zu untersuchenden Wassers geführt wird.

Konzentrationen von einer Größenordnung von 0.0001% in indifferenten Gasen und 1/μg/l in Wasser lassen sich nach dieser Methode mit genügender Genauigkeit bestimmen.

BIBLIOGRAPHIE

- ¹ J. B. SMITH, E. K. GILBERT ET M. P. HOWIE, *Anal. Chem.*, 26 (1954) 667.
- ² R. D. GOODWIN, *Anal. Chem.*, 25 (1953) 263; *Nalco Abstracts*, Jan. Feb. March (1956); C. A. NOLL ET J. W. POLSKY, *Techn. Assoc. Pulp & Paper Ind.*, 39 (1) (1956) 51.
- ³ H. E. HÖMIG, *Mitt. Ver. Grosskesselbesitzer*, 25 (1953) 521.
- ⁴ L. BLUM ET L. EDELHAUSEN, *Anal. Chim. Acta*, 13 (1955) 120.
- ⁵ H. M. GIFFT, *Water Sewage Works*, 91 (12) (1944) 427.
- ⁶ H. E. HÖMIG, *Mitt. Ver. Grosskesselbesitzer*, 48 (1957) 170.
- ⁷ W. K. LEWIS ET W. G. WHITMAN, *Ind. Eng. Chem.*, 16 (1924) 1215.
- ⁸ M. KH. KISHINEVSKII ET L. A. MOCHALOVA, *Uch. Zap. Kishinevsk. Gos. Univ.*, 14 (1954) 31; *C.A.*, (1958) 3416; *Zh. Prikl. Khim.*, 28 (1955) 927; *C.A.*, (1956) 5372.
- ⁹ R. A. T. O. NIJSING, R. H. HENDRIKSZ ET H. KRAMERS, *Chem. Eng. Sci.*, 10 (1959) 88.
- ¹⁰ R. T. HASLAM, R. L. HERSHEY ET R. H. KEEN, *Ind. Eng. Chem.*, 16 (1924) 1224.

Anal. Chim. Acta, 29 (1963) 1-9

GRAVIMETRIC DETERMINATION OF COBALT AS PRESUMED
 $K_3Co(NO_2)_6$

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(Received January 16th, 1963)

Since first described by DUFLOS AND FISCHER¹ in 1847 the precipitation of cobalt as yellow 'potassium cobaltinitrite' according to the reaction:



has been commonly used as a means of separating cobalt from nickel and many other metallic elements. The remarkable efficiency of the separation has most recently been demonstrated by KALLMANN².

However, the gravimetric determination of cobalt based on weighing the precipitate has never gained favor; indeed, it has not even been seriously investigated. Well-known reference books of analytical chemistry³⁻⁷ all recommend that the precipitate be decomposed and dissolved, and the cobalt content be determined electrogravimetrically or by some other method. Current opinion is well exemplified by the statement: 'The precipitate is never weighed as such, nor is it titrated as in some modifications of the corresponding method for potassium', which appeared in the original 1929 edition of HILLEBRAND *et al.*, which is repeated in the second 1953 edition³, and which also is found in the recent second edition (1960) of the American Chemical Society monograph on cobalt⁷. Since we have been unable to find any reference to a critical study of the composition of the precipitate, it appears that this opinion has been propagated because of the well-known shortcomings of the potassium determination by the cobaltinitrite method.

When potassium is determined by employing sodium cobaltinitrite as reagent to precipitate approximately $K_2NaCo(NO_2)_6 \cdot xH_2O$, it is indeed difficult to control conditions to obtain a precipitate in which the K/Na ratio is exactly 2. Furthermore the degree of hydration is variable. DUVAL⁸ has very clearly reviewed these difficulties of the potassium determination. However, when cobalt is determined, the situation is quite different because no sodium need be present, and the tri-potassium salt rather than a mixed potassium-sodium salt is precipitated.

There is no agreement in the literature as to whether or not the tri-potassium salt is hydrated. Most reference monographs³⁻⁷ write its formula as ' $2 K_3Co(NO_2)_6 \cdot 3H_2O$ ', and in his recent review of the analytical chemistry of cobalt, WILLIAMS⁹ also assumes this hydrated formula. However, SWIFT¹⁰ and KOLTHOFF AND SANDELL¹¹ write the anhydrous formula. We have not found evidence in the literature for either formula. DUVAL¹² studied the thermogravimetric curve of the salt, which he states was pre-

pared by the method of BRAUNER¹³. Actually, BRAUNER did not describe how he precipitated the tri-potassium salt, and his conclusion that the salt he studied contained 13.72% cobalt corresponds more closely to $K_2NaCo(NO_2)_6$ (13.52% cobalt) than to $K_3Co(NO_2)_6$ (13.03% cobalt). Presumably DUVAL meant to quote BRUNCK¹⁴, who seems to have originated the procedure most commonly used for precipitating the tri-potassium salt (acetic acid solution of pH *ca.* 4, with a large excess of potassium nitrite). DUVAL's thermogravimetric curve demonstrates that the tri-potassium salt is stable up to 160°, but it does not, of course, indicate whether or not the salt is hydrated. In contrast to the tri-potassium salt, DUVAL reported that the mixed sodium-potassium salt loses weight more or less continuously on heating, and the thermolysis curve was not reproducible. Contradictorily, CUMBERS AND COPPOCK¹⁵ claimed that the mixed sodium-potassium salt was stable on heating up to 180°.

A long-held misconception is that complete precipitation of $K_3Co(NO_2)_6$ requires a very long time, and this has recently been dispelled by SALYER AND SWEET¹⁶. Using radioactive cobalt to follow the rate of disappearance of cobalt from the solution, and the most commonly used conditions of an acetic acid solution and a large excess of potassium nitrite, SALYER AND SWEET found that the rate of precipitation is inversely dependent on temperature. They demonstrated that at 20° precipitation is complete within an hour provided that a large enough concentration of potassium nitrite is present. SALYER AND SWEET did not weigh the precipitate nor investigate its composition.

Apparently the only previous study of a cobaltinitrite precipitate as a weighing form for the determination of cobalt is that of CUMBERS AND COPPOCK¹⁵. These authors precipitated approximately ' $K_2NaCo(NO_2)_6 \cdot H_2O$ ' by using a reagent containing much more sodium than potassium (Na/K ratio between 15/1 and 40/1). They found that the weight of the precipitate (after drying at 120°) corresponded to ' $K_2NaCo(NO_2)_6 \cdot H_2O$ ' only when the temperature during precipitation had been closely controlled at 60°. A variation of only 2° changed the weight of the precipitate by 0.1%. They reported that the water content of the precipitate (directly determined after initially drying at 120°) varied from 1.3% when precipitation was made at 100°, to 4.8% after precipitation at 20°, compared to the theoretical value 3.9% for $K_2NaCo(NO_2)_6 \cdot H_2O$. CUMBERS AND COPPOCK did not determine the K/Na ratio in the precipitates. Furthermore, in all their experiments only a single quantity of cobalt (65 mg) was used, so no information was obtained on the probable variation of the composition of the precipitate with the amount of cobalt precipitated. The study of CUMBERS AND COPPOCK emphasizes the serious shortcomings of the mixed sodium-potassium salt as a weighing form for cobalt.

The present investigation is concerned with the tri-potassium salt, whose properties are much more suitable than the mixed sodium-potassium salt. In addition to determination of the weights of precipitate obtained with widely varying quantities of cobalt under various conditions of precipitation, the precipitates have also been analyzed to ascertain their actual composition.

EXPERIMENTAL

The cobalt standard used in this study was spectrographically pure cobalt wire manufactured by Johnson, Matthey and Co., Ltd., London, and obtained through

Jarrell-Ash Co., Newtonville, Mass. The certificate of spectrographic analysis furnished by the manufacturer reported 5 p.p.m. nickel, 3 p.p.m. silicon, and 1 p.p.m. each of copper, iron, and silver. Forty other elements were sought but were not detected.

Standard cobalt solutions by weight were prepared by dissolving carefully weighed samples of the pure cobalt wire in hot (but not boiling) 1:1 hydrochloric acid with precautions to avoid 'spray loss'. The solution was then evaporated to dryness on the steam bath. The residue of cobaltous chloride was treated with a small known amount of hydrochloric acid and was then dissolved in water and diluted to a known weight. The several standard solutions so prepared contained between 2 and 5 mg of cobalt per g of solution, and the concentration of free hydrochloric acid ranged from 0.005 to 0.01 *M*. Samples of these standard cobalt solutions were dispensed by weight to ± 1 mg. By this technique the uncertainty in the quantity of 'cobalt taken' was believed to be less than ± 0.01 mg.

Weighings were made with a weight set which had been recently calibrated by the 'internally consistent' Richards method.

The potassium nitrite used was Mallinckrodt 'analytical reagent'. Stock 50% solutions in water (0.5 g KNO_2 per ml) were prepared and filtered. Such filtered stock solutions remained clear and stable for several months when stored in a Pyrex bottle. All other reagents were of 'analytical reagent' quality.

ANALYTICAL PERFORMANCE DATA

The gravimetric determination of cobalt as 'potassium cobaltinitrite' was tested according to the following procedure, in which the precipitation conditions correspond closely to those most commonly recommended in the literature.

The cobalt standard solution (containing no more than 0.01 *M* hydrochloric acid) was weighed into a 150-ml beaker and diluted to 50 ml. The solution was acidified with glacial acetic acid and 30 ml of 50% potassium nitrite solution (15 g of KNO_2) was added rapidly with good stirring. The mixture was re-stirred several times over a period of about 30 min, and the precipitate was then allowed to settle.

The amount of glacial acetic acid (17 *M*) added was either 5 or 10 ml, the latter being equivalent to the 15 g of potassium nitrite present according to the reaction:



Since acetic acid ($\text{p}K = 4.74$) is considerably weaker than nitrous acid ($\text{p}K = 3.35$) the equilibrium constant for this reaction is small, *viz.*

$$K = \frac{(\text{HNO}_2)(\text{CH}_3\text{COO}^-)}{(\text{NO}_2^-)(\text{CH}_3\text{COOH})} = 4.0 \cdot 10^{-2}$$

Hence, when equivalent quantities of acetic acid (10 ml of 17 *M*) and potassium nitrite (15 g) are mixed, about one-fifth of the total nitrite is present as nitrous acid and the pH of the solution is close to 4.0. Because in neutral solution the rate of formation of $\text{Co}(\text{NO}_2)_6^{3-}$ ion is very slow, but is rapid when the solution is slightly acidic, it is evident that nitrous acid rather than nitrite ion is the active oxidant. Consequently the pH must small enough to provide an ample concentration of nitrous acid. On the other hand, the pH must be large enough to maintain a large concentra-

tion of free nitrite ion to favor the formation of $\text{Co}(\text{NO})_2^{2-}$. A pH between 4 and 4.5 is an optimum compromise, and is obtained when 5 to 10 ml of glacial acetic are added per 15 g of potassium nitrite in a final volume of 85 to 100 ml.

The precipitate was usually allowed to stand overnight in contact with the mother solution before filtration. Actually, however, such a long time is unnecessary. SALYER AND SWEET¹⁶ employed radioactive cobalt to follow the rate of precipitation of potassium cobaltinitrite under conditions essentially the same as in this study. They reported that the rate of precipitation was inversely proportional to temperature, and that at 20° precipitation was complete within about one hour. In confirmation of this we found that the weight of precipitate obtained after two hours standing at room temperature (24–26°) was the same as on longer standing.

The precipitate was collected on a tared, medium porosity sintered glass filtering crucible. Complete transfer from the precipitation beaker, and preliminary washing, were effected with 100 ml of 2% potassium nitrite solution. The precipitate was finally washed with five 10 ml portions of 80% ethanol, and one 10 ml portion of acetone. It was weighed after drying in an oven for 1 h at 110°.

The solubility of potassium cobaltinitrite is not known exactly, and it would not be easy to evaluate because saturated solutions of the salt in water are unstable. A saturated solution becomes colorless within 30 min at room temperature, presumably because of reduction of the cobalt(III) by water. Consequently the solubility value, 89 mg/100 ml of water at 17°, quoted in handbooks, which appears to stem from the measurements of ROSENBLADT¹⁷, must be much larger than the true value. This is evident from the following experiment. A dried sample of the salt (0.5545 g) in a sintered glass crucible was washed with 100 ml of water at *ca.* 25° over a period of 10 min, and during this time the salt was kept stirred up with the water. The salt was then finally washed with 10 ml of acetone, redried at 110°, and weighed. The loss in weight was 3.7 mg. When the same sample of the salt was then washed in the same way with 50 ml of 80% ethanol, the loss in weight was 0.25 mg. When washed *seriatim* with 100 ml of 2% potassium nitrite solution, 50 ml of 80% ethanol, and 10 ml of acetone (the procedure finally adopted) the loss in weight was 0.30 mg, which corresponds to only 0.04 mg of cobalt.

The drying temperature of 110° was chosen because the thermogravimetric curve measured by DUVAL shows that the weight is constant up to 160°, and thus 110° is ample to remove surface moisture. After a final washing with acetone and air-drying, we observed that the salt loses only 0.1% in weight on drying for 1 h at 110°.

Results obtained by the foregoing procedure with widely varying amounts of cobalt are summarized in Table I. The 'cobalt found', and corresponding percentage error, were calculated on the assumption that the dried precipitate has the formula $\text{K}_3\text{Co}(\text{NO}_2)_6$ with 13.031% cobalt. Correction was made for the small washing loss described above.

In Fig. 1 the deviation of the weight of the precipitate from $\text{K}_3\text{Co}(\text{NO}_2)_6$ is plotted against the quantity of cobalt taken for series A, B, C, and F of Table I. The striking characteristic of all four series is the decrease of the deviation as the amount of cobalt increases, and its change of sign from positive to negative in series A, B, and C. It may be noted that if the precipitate were $\text{K}_3\text{Co}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$ the positive deviation would be +3.83%, and if it were the oft-quoted ' $2\text{K}_3\text{Co}(\text{NO}_2)_6 \cdot 3\text{H}_2\text{O}$ ' the deviation would be +5.65%.

TABLE I
DETERMINATION OF COBALT AS PRESUMED $K_3Co(NO_2)_6$ *

<i>Co taken</i> (mg)	<i>Ppt.</i> (g)	<i>Co found</i> (mg)	<i>Deviation from</i> $K_3Co(NO_2)_6$ (%)
(A) Initial pptn. at 70°, and 10 ml glacial acetic acid.			
12.21	0.0958	12.48	+2.19
27.49	0.2170	28.26	+2.88
50.91	0.3960	51.61	+1.38
100.79	0.7760	101.12	+0.33
127.14	0.9767	127.28	+0.12
269.55	2.0544	267.71	-0.68
(B) Initial pptn. at 70°, and 5 ml glacial acetic acid.			
26.71	0.2104	27.42	+2.66
55.81	0.4316	56.24	+0.78
126.46	0.9707	126.50	+0.03
229.00	1.7465	227.59	-0.62
(C) Pptn. at room temp. (22-26°), and 5 ml glacial acetic acid.			
25.79	0.2013	26.23	+1.70
46.82	0.3621	47.19	+0.78
74.39	0.5725	74.61	+0.27
104.64	0.8020	104.51	-0.20
147.39	1.1283	147.03	-0.25
207.40	1.5804	205.95	-0.70
279.89	2.1273	277.22	-0.95
(D) Pptn. at 0°, and 5 ml glacial acid.			
265.82	1.9224	250.48	-5.78
(E) Rapid reverse pptn. at 70°, and 5 ml glacial acetic acid.			
25.79	0.2038	26.56	+2.99
229.30	1.7527	228.40	-0.39
(F) Very slow reverse pptn. at room temp., and 5 ml glacial acetic acid.			
41.24	0.3235	42.16	+2.23
128.79	0.9954	129.71	+0.71
269.59	2.0699	269.74	+0.06
(G) Very slow direct pptn. at room temp., and 5 ml glacial acetic acid.			
26.66	0.2020	26.45	-0.79
259.21	1.9336	251.98	-2.79

* In all cases the initial volume of the cobalt solution was 50 ml and 30 ml of 50% potassium nitrite solution (15 g KNO_2) was used. The quantity 'cobalt found' was calculated on the assumption that the precipitate is $K_3Co(NO_2)_6$ after drying at 110°.

That the negative error with the larger amounts of cobalt in series A, B, and C is not caused by incomplete precipitation was established by determining the cobalt remaining in several of the filtrates. The filtrates were evaporated to dryness with excess of hydrochloric acid, and the cobalt was then determined spectrophotometrically with nitroso-R salt. In no case did the amount of cobalt exceed 0.03 mg.

Whether the precipitation was made from an initially hot solution or at room temperature had little influence on the weight of precipitate with a given amount of cobalt, provided that the mixture stood for at least 2 h at room temperature before the precipitate was filtered off. Thus, there is no justification for the oft-repeated recommendation that the precipitation be made from a hot solution; this only retards the precipitation.

Varying the amount of glacial acetic acid present from 5 to 10 ml (one-half to fully the equivalent of the 15 g of potassium nitrite used) had no effect. However, when the amount of acetic acid was increased to 20 ml (twice the equivalent of the potassium nitrite) a negative error of -1.7% was observed with 50 mg of cobalt and -2.1% with 250 mg of cobalt. With excess of acetic acid the precipitate was so finely divided that it tended to run through the medium porosity sintered glass filter.

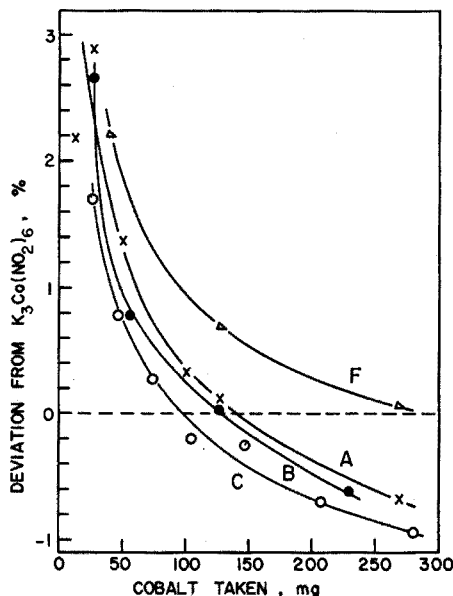


Fig. 1. Deviation of weight of the precipitate from $K_3Co(NO_2)_6$ as a function of the quantity of cobalt precipitated. The letters on each curve correspond to those given in Table I.

When the precipitation was done in an ice-cold solution (experiment *D* of Table I) the weight of precipitate was much smaller than that obtained at room temperature. Although the amount of cobalt in the filtrate in this trial was not determined, the absence of color in the filtrate indicated that this large negative error was not caused by incomplete precipitation. We believe that it is due to incomplete oxidation of the cobalt to the trivalent state, and precipitation of part of the cobalt in the divalent state as a potassium cobaltous nitrite salt.

In the experiments under *E* in Table I, the cobalt solution was added to the previously acidified, and hot, potassium nitrite solution over a period of about 1 min. With this relatively rapid reverse precipitation from a hot solution the weight of the precipitate was only slightly larger than for precipitation with the usual order of mixing the solutions (compare with series *B*). However, as shown by the trials under *F*, very slow reverse precipitation at room temperature caused a marked increase in the weight of the precipitate (compare with series *C*). In the experiments under *F* the cobalt solution was diluted to 50 ml and added to the acidified potassium nitrite solution at a rate of only 1 ml per min from an ordinary glass funnel whose stem had

been drawn down to a capillary tip. The potassium nitrite solution was kept well stirred with a mechanical stirrer during the 50 min that elapsed for complete addition of the cobalt solution.

In contrast to slow reverse precipitation, very slow direct precipitation at room temperature caused a marked decrease in the weight of the precipitate, as shown by the two trials under *G*. In these trials the acidified potassium nitrite solution was added dropwise over a period of 20 min to the cobalt solution which was stirred mechanically.

All of the experiments in Table I were performed with the same amount of potassium nitrite present (15 g). Additional trials showed that increasing the amount of potassium nitrite had relatively little (if any) effect. For example, when 285 mg of cobalt was precipitated as in series *F*, except that 100 ml rather than 30 ml of the 50% potassium nitrite was used (with 17 ml instead of 5 ml of acetic acid) the deviation was -0.07% , compared to $+0.06\%$ with the same amount of cobalt in series *F*. When 28 mg of cobalt was precipitated, using 100 ml of 50% potassium nitrite solution, the deviation was $+4.7\%$, which is not much different than one would expect from an extrapolation of curve *F* in Fig. 1 down to 28 mg of cobalt.

The effect of increasing the total volume of the solution (using 15 g of KNO_2) was also investigated. When 275 mg of cobalt was precipitated as in series *F*, except that the 30 ml of 50% potassium nitrite solution was diluted to 100 ml before the cobalt solution was slowly added, the deviation was -0.77% compared to $+0.06\%$ in series *F*. Under the same conditions with 24 mg of cobalt the deviation was $+0.74\%$. Hence precipitation from a larger volume definitely decreased the weight of the precipitate, but the range of the deviation from $\text{K}_3\text{Co}(\text{NO}_2)_6$ with the amount of cobalt was not much different than in series *F*.

Because it was thought that chloride ion from the cobaltous chloride standard solutions might be responsible for the trend shown by the curves in Fig. 1, a series of trials was run with a standard cobaltous sulfate solution. The results were the same as with the standard cobaltous chloride solutions.

Composition of the potassium cobaltinitrite precipitate

Because the precipitation of cobalt was found to be complete, it is evident that the change in the ratio of the weight of precipitate to weight of cobalt with the quantity of cobalt taken must result from variation in the composition of the precipitate. The increasing positive error (based on presumed $\text{K}_3\text{Co}(\text{NO}_2)_6$) with decreasing quantities of cobalt can be ascribed to a mixture of the anhydrous salt and some hydrated salt. The negative error in series *A*, *B*, and *C* with amounts of cobalt greater than about 150 mg (in spite of complete precipitation of the cobalt) must result from the precipitation of a mixture of salts containing potassium, cobalt (in both the di- and tri-valent oxidation states), nitrite, and possibly water, in which the percentage of cobalt is greater than that for $\text{K}_3\text{Co}(\text{NO}_2)_6$. In other words, the average formula weight of the mixed precipitate must be smaller than that of $\text{K}_3\text{Co}(\text{NO}_2)_6$.

To identify the other salts of potassium, cobalt, nitrite, and water that accompany $\text{K}_3\text{Co}(\text{NO}_2)_6$, precipitates obtained with both very small (25 mg) and relatively large (250 mg) quantities of cobalt were analyzed. The precipitates were prepared as in series *B* of Table I, *i.e.*, initial temperature *ca.* 70° , 5 ml of glacial acetic, and 15 g of potassium nitrite in a final volume of 85 to 100 ml. The precipitates were washed

by the same technique used to obtain the data in Table I, and they were finally dried for 1 h at 110° before analysis.

The precipitates were analyzed for potassium and water, and in addition their cobalt content was known from the data of part *B* of Table I. No attempt was made to determine either the nitrite or total nitrogen content because the percentage of nitrogen in the salts likely to be present varies relatively little, and methods of nitrite or nitrogen determination are not precise enough under this condition to provide meaningful information.

To determine water, samples of about 1 g in a silica combustion boat in a glass tube in an electric tube furnace were decomposed by gradual heating to ca. 500° in an atmosphere of pure, dried nitrogen. The water vapor was swept from the combustion tube with dry nitrogen, and collected in anhydrous magnesium perchlorate in a tared drying tube. The gain in weight of the magnesium perchlorate was assumed to be due to absorbed water. Of the several water absorbents that might have been used, magnesium perchlorate was selected because CUMBERS AND COPPOCK reported that it does not absorb oxides of nitrogen, and our experience confirmed this. Before use, the magnesium perchlorate was exposed for several days to hydrogen chloride gas in a desiccator to ensure that it was free of any basic salt that might have absorbed the acidic oxides of nitrogen.

To determine potassium, the ignition residue from the water determination was leached repeatedly with water. The leachate was evaporated three to six times with excess of hydrochloric acid in a silica beaker and finally in a silica crucible. The residue of potassium chloride (0.2 to 0.3 g) was weighed after drying at 500°. Colorimetric tests with nitroso-R salt demonstrated that the amount of cobalt in the potassium chloride was less than 0.05 mg, and hence negligible. The amount of potassium remaining unextracted in the cobalt oxides after leaching was determined by dissolving the cobalt oxides in hydrochloric acid and determining the potassium in the resulting solution by means of a flame photometer. The quantity of potassium so found ranged from 0.2 to 0.8 mg per 100 to 150 mg of the cobalt oxides, and corresponded to 0.1 to 0.4% of the total potassium. The appropriate correction was applied in each determination.

The cobalt content of the precipitates was calculated from the observed weights of the precipitates obtained with the known amounts of cobalt taken (and completely precipitated) via the data in part *B* of Table I.

Table II summarizes the results of these analyses. The designation under 'sample' of '25 mg' and '250 mg' means that the precipitates had been obtained with 25 mg and 250 mg of cobalt respectively under the conditions of part *B* of Table I. In each case four separate samples were analyzed and the average deviation from the mean is indicated.

To facilitate interpretation of the analyses in Table II, we have summarized in Table III the theoretical compositions of the compounds most likely to accompany $K_3Co(NO_2)_6$ in the precipitates.

The percentage of water (2.47) found in the precipitate obtained with 25 mg samples cobalt agrees closely with the observed deviation (+2.7%) of the weight of the precipitate from $K_3Co(NO_2)_6$ (see Table I and Fig. 1). From the observed percentages of potassium and cobalt, the molar ratio K/Co for this precipitate is 3.016 ± 0.012 , or 3 within the experimental uncertainty of $\pm 0.4\%$. These data

TABLE II
ANALYSES OF 'POTASSIUM COBALTINITRITE' PRECIPITATES^a

Sample	H ₂ O (%)	K (%)	Co (%)
'25 mg'	2.47 ± 0.01 (1.37)	25.41 ± 0.09 (6.50)	12.70 (2.155)
'250 mg'	2.88 ± 0.02 (1.60)	25.00 ± 0.10 (6.39)	13.12 (2.226)

^a The values in parentheses under each percentage figure are mmoles/g of sample.

TABLE III
THEORETICAL COMPOSITIONS OF PERTINENT COMPOUNDS OF POTASSIUM, COBALT, NITRITE AND WATER

Substance	Formula weight	H ₂ O (%)	K (%)	Co (%)
K ₃ Co(NO ₂) ₆	452.29	—	25.96	13.03
K ₃ Co(NO ₂) ₆ · H ₂ O	470.31	3.83	24.95	12.53
K ₃ Co(NO ₂) ₆ · 1.5H ₂ O	479.33	5.65	24.48	12.30
K ₃ Co(NO ₂) ₆ (H ₂ O)	385.2	4.68	20.30	15.30
K ₂ Co(NO ₂) ₄	321.2	—	24.35	18.35
K ₂ Co(NO ₂) ₅ (NO)	397.20	—	19.69	14.84

strongly support the conclusion that with relatively small amounts of cobalt the precipitate is a mixture of anhydrous and hydrated K₃Co(NO₂)₆.

The water must be present as hydrate water in the crystal rather than water coordinated directly to cobalt, as, for example, in the hypothetical salt K₂Co(NO₂)₅(H₂O). The formula weight of this salt is much smaller than that of K₃Co(NO₂)₆ (see Table III), so that if it were present the observed weight of the precipitate would have been *smaller* than for K₃Co(NO₂)₆ rather than larger as actually observed.

The particular hydrate cannot, as yet, be identified. Such identification would require an independent determination of the relative amounts of the two solid phases, and we do not know how such a determination could be made in view of the fact that practically nothing is known about the physical properties of either phase. However, if we *assume* a mixture of K₃Co(NO₂)₆ and K₃Co(NO₂)₆ · H₂O, it follows from the water analysis that the proportion of the monohydrate would be 64.5%, from which the theoretical potassium content is 25.31%. The observed potassium content (25.41 ± 0.09%) agrees well with this value, demonstrating that the water and potassium analyses are mutually consistent, but equally good agreement would result for a mixture of some other hydrate and the anhydrous salt.

The precipitate obtained with 250 mg samples of cobalt contains more water, less potassium, and more cobalt, than that obtained with 25 mg samples of cobalt. The observed percentages of potassium and cobalt correspond to a molar ratio K/Co of 2.872 ± 0.012, which definitely indicates the presence of compounds containing

potassium and cobalt in a 2/1 molar ratio admixed with compounds in which this ratio is 3/1. A 2/1 value for K/Co means that the cobalt must either be present in the divalent oxidation state, as, for example, in $\text{K}_2\text{Co}(\text{NO}_2)_4$, or that the cobalt is in the trivalent state but that water replaces nitrite ion in the coordination sphere, as, for instance, in $\text{K}_2\text{Co}(\text{NO}_2)_5(\text{H}_2\text{O})$. However, the presence of the latter compound is ruled out because its potassium content (20.3%) is much too small for reconciliation with the observed percentages of water (2.88%) and potassium (25.00%). A decrease below 3 of the K/Co ratio would also result if nitrosyl replaced nitrite ion, as, for instance, in $\text{K}_2\text{Co}(\text{NO}_2)_5(\text{NO})$, but the percentage of potassium in this compound (19.69%) is so small compared to the observed value (25.00%) that its presence seems highly unlikely.

We conclude that the decrease in the weight of the precipitate below that for $\text{K}_3\text{Co}(\text{NO}_2)_6$ with large amounts of cobalt is caused by incomplete oxidation of the cobalt to the trivalent state and the precipitation of the unoxidized divalent cobalt as $\text{K}_2\text{Co}(\text{NO}_2)_4$. A mixture of 75% $\text{K}_3\text{Co}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$, 15% $\text{K}_3\text{Co}(\text{NO}_2)_6$, and 10% $\text{K}_2\text{Co}(\text{NO}_2)_4$, would correspond to the observed percentages of water, potassium, and cobalt found in the precipitate obtained with a 250 mg sample of cobalt. However, a mixture of different proportions containing hydrated $\text{K}_2\text{Co}(\text{NO}_2)_4$, some other hydrate of $\text{K}_3\text{Co}(\text{NO}_2)_6$, and anhydrous $\text{K}_3\text{Co}(\text{NO}_2)_6$, could also account for the analytical data. The essential element of our conclusion is that the precipitate contains both hydrated and anhydrous $\text{K}_3\text{Co}(\text{NO}_2)_6$, together with a potassium cobaltous nitrite, such as $\text{K}_2\text{Co}(\text{NO}_2)_4$, which may be either anhydrous or hydrated.

Binary mixtures containing only hydrated $\text{K}_3\text{Co}(\text{NO}_2)_6$ and either hydrated or anhydrous $\text{K}_2\text{Co}(\text{NO}_2)_4$ (*i.e.*, no anhydrous $\text{K}_3\text{Co}(\text{NO}_2)_6$) could yield the weights of precipitate observed with all amounts of cobalt taken. However, if no anhydrous $\text{K}_3\text{Co}(\text{NO}_2)_6$ were present the percentage of potassium would be smaller than 24.95% (the value for $\text{K}_3\text{Co}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$). Because with both large and small amounts of cobalt the observed percentage of potassium in the precipitates is *larger* than this, and because anhydrous $\text{K}_3\text{Co}(\text{NO}_2)_6$ is the only likely compound whose potassium content is greater than 24.95% (see Table III), we conclude that anhydrous $\text{K}_3\text{Co}(\text{NO}_2)_6$ must be present.

Although we have only analyzed precipitates obtained under the conditions of series *B* in Table I, it seems evident that the precipitates obtained under the other conditions must also consist of a mixture of anhydrous and hydrated $\text{K}_3\text{Co}(\text{NO}_2)_6$, and with large amounts of cobalt, some $\text{K}_2\text{Co}(\text{NO}_2)_4$ due to incomplete oxidation of the cobalt(II). The increase in the relative weight of the precipitate with decreasing quantities of cobalt under all conditions is interpreted as due to more complete oxidation of the cobalt as its amount is decreased, and hence a decrease in the proportion of $\text{K}_2\text{Co}(\text{NO}_2)_4$. Precipitation at 0° would be expected to decrease the rate of oxidation of cobalt(II) by nitrous acid, to favor the precipitation of slightly soluble compounds of cobalt(II) (*e.g.*, $\text{K}_2\text{Co}(\text{NO}_2)_4$), and thus to cause a relatively large negative deviation of the weight of the precipitate from $\text{K}_3\text{Co}(\text{NO}_2)_6$, as observed in the experiment under *D* in Table I. Conversely, when the cobalt solution is added very slowly to the acidified potassium nitrite solution (as in series *F* of Table I) more complete oxidation of the cobalt(II) is favored, less $\text{K}_2\text{Co}(\text{NO}_2)_4$ precipitates, and the weight of the precipitate increases.

CONCLUSIONS

The foregoing data emphasize that the composition of 'potassium cobaltinitrite' varies with the quantity of cobalt precipitated, but they also demonstrate that the deviation of the weight of the precipitate from $K_3Co(NO_2)_6$ is small enough to justify the application of this simple gravimetric method in practical analyses. For example, under the conditions of series C of Table I and Fig. 1, the deviation from presumed $K_3Co(NO_2)_6$ ranges only from +1% with 40 mg of cobalt to -1% with 300 mg of cobalt. Furthermore, the weight of precipitate obtained with a given quantity of cobalt is so reproducible (*ca.* $\pm 0.1\%$) that an empirical 'gravimetric factor' can be applied to decrease the error to a small fraction of 1%. Few methods of cobalt determination are more trustworthy than this.

The electrogravimetric determination of cobalt appears to be the most favored method of concluding a cobalt determination after preliminary separation as potassium cobaltinitrite. SALYER AND SWEET¹⁸ recently studied ten of the most commonly recommended procedures for the electrogravimetric determination of cobalt, and their results show that all of the procedures are subject to a positive error which ranges rather erratically from a few tenths of a milligram to as much as 2 mg when 50 mg of cobalt is deposited. This error is as large as, or larger than, if the precipitate is simply weighed as presumed $K_3Co(NO_2)_6$.

KALLMANN² employed precipitation as potassium cobaltinitrite from a tartrate-containing solution to separate cobalt 'from virtually any combination of elements encountered in the metallurgical field'. He did not weigh the precipitate but concluded the determination electrogravimetrically, or colorimetrically with nitroso-R salt. The procedures given by KALLMANN for the analysis of various types of cobalt-containing materials should be very useful in practical analyses, but from the present study it is evident that the laborious electrogravimetric concluding determination is quite unnecessary. When KALLMANN's procedures for the precipitation are used, we have found that considerable potassium hydrogen tartrate precipitates along with the potassium cobaltinitrite. Hence the original precipitate should be dissolved and reprecipitated under the optimum conditions found in this study (series C of Table I).

Appreciation is expressed to the National Science Foundation for a fellowship held by one of us (P.J.L.).

SUMMARY

The composition of 'potassium cobaltinitrite' precipitated under the usual conditions from a slightly acid solution containing a large excess of potassium nitrite, and finally dried at 110°, has been determined. When a relatively small quantity of cobalt is precipitated the dried precipitate consists of a mixture of anhydrous and hydrated $K_3Co(NO_2)_6$. With large amounts of cobalt the precipitate also contains a salt of cobalt(II) (probably $K_2Co(NO_2)_4$) due to incomplete oxidation of the cobalt(II). Because the formula weight of $K_2Co(NO_2)_4$ is smaller than that of $K_3Co(NO_2)_6$, whereas that of hydrated $K_3Co(NO_2)_6$ is larger, the weight of the precipitate is actually not very different than if it were pure $K_3Co(NO_2)_6$. Quantities of cobalt from 40 to 300 mg can be determined with an error within $\pm 1\%$ by weighing the dried precipitate as presumed $K_3Co(NO_2)_6$, and, if desired, the error can be decreased to a few tenths of a percent by employing an empirical factor. This simple method rivals in accuracy the more laborious electrogravimetric method.

RÉSUMÉ

Les auteurs ont déterminé la composition du cobaltinitrite de potassium, précipité dans les conditions usuelles: à partir de solutions légèrement acides, renfermant un grand excès de nitrite de potassium, avec séchage à 110°. Pour les relativement petites quantités de cobalt, le précipité

obtenu est formé d'un mélange de $K_3Co(NO_2)_6$ anhydre et hydraté. Pour de fortes teneurs en cobalt, le précipité renferme également un sel de cobalt(II), probablement $K_2Co(NO_2)_4$, provenant d'une oxydation incomplète du cobalt. Cependant, des quantités de cobalt de 40 à 300 mg peuvent être dosées avec une erreur de 1%; on peut même ramener l'erreur à quelques dixièmes de % en utilisant un facteur empirique. Cette méthode relativement simple, peut rivaliser avec la méthode électrogravimétrique moins rapide.

ZUSAMMENFASSUNG

Es wurde die Zusammensetzung des Kalium-kobaltinitrit, das unter den gewöhnlichen Bedingungen aus schwach saurer Lösung in Gegenwart eines grossen Ueberschusses an Kaliumnitrit gefällt und bei 110° getrocknet wurde, untersucht. Wenn eine verhältnismässig kleine Menge Kobalt gefällt wird, besteht der getrocknete Niederschlag aus einem Gemisch von wasserfreiem und hydratisiertem $K_3Co(NO_2)_6$. Bei grossen Kobaltmengen enthält der Niederschlag auch ein Salz des Kobalts-(II) (vermutlich $K_2Co(NO_2)_4$) infolge unvollständiger Oxydation des Kobalts-(II). Während das Gewicht des $K_2Co(NO_2)_4$ kleiner ist als das des $K_3Co(NO_2)_6$, dagegen das des hydratisierten $K_3Co(NO_2)_6$ grösser, so ist das Gewicht des Niederschlages nicht sehr verschieden von dem des reinen $K_3Co(NO_2)_6$. Kobaltmengen von 40 bis 300 mg können mit einem Fehler von ungefähr $\pm 1\%$ bestimmt werden unter der Annahme, dass der getrocknete Niederschlag aus $K_3Co(NO_2)_6$ besteht. Dieser Fehler kann auf einige zehntel Prozent reduziert werden durch Anwendung eines empirischen Faktors. Diese einfache Methode ergibt ungefähr die gleiche Genauigkeit wie die umständlichere elektrogravimetrische Methode.

REFERENCES

- 1 A. DUFLOS AND N. W. FISCHER, *Pogg. Ann.*, 72 (1847) 477; N. W. FISCHER, *Pogg. Ann.*, 74 (1848) 124.
- 2 S. KALLMANN, *Anal. Chem.*, 22 (1950) 1519.
- 3 W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT AND J. I. HOFFMAN, *Applied Inorganic Analysis*, 2nd Ed., J. Wiley, New York, 1953.
- 4 G. E. F. LUNDELL, J. I. HOFFMAN AND H. A. BRIGHT. *Chemical Analysis of Iron and Steel*, New York, 1931.
- 5 W. W. SCOTT, *Standard Methods of Chemical Analysis*, N. H. FURMAN, 5th Ed., Ed. D. Van Nostrand, New York, 1939.
- 6 K. GEORGI *et al.*, in *Analyse der Metalle. Schiedsverfahren*, Springer-Verlag, Berlin, 1942.
- 7 R. S. YOUNG, *Cobalt. Its Chemistry, Metallurgy, and Uses*, 2nd Ed., Am. Chem. Soc. Monograph Series, Reinhold, New York, 1960.
- 8 C. DUVAL, *Traité de Micro-analyse Minérale*, Tome I, Presses Scientifiques Internationales, Paris, 1954, p. 188 et 193.
- 9 W. J. WILLIAMS, *Talanta*, 1 (1958) 88.
- 10 E. H. SWIFT, *A System of Chemical Analysis*, Prentice-Hall, New York, 1950.
- 11 I. M. KOLTHOFF AND E. B. SANDELL, *Textbook of Quantitative Inorganic Analysis*, MacMillan, New York, 1953.
- 12 C. DUVAL, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, 1953.
- 13 B. BRAUNER, *Z. Anal. Chem.*, 16 (1877) 195.
- 14 O. BRUNCK, *Z. Angew. Chem.*, 20 (1907) 1847.
- 15 C. F. CUMBERS AND J. B. M. COPPOCK, *J. Soc. Chem. Ind. (London)*, 56T (1937) 405.
- 16 D. SALYER AND T. R. SWEET, *Anal. Chem.*, 32 (1960) 548.
- 17 T. ROSENBLADT, *Ber.*, 19 (1886) 2535.
- 18 D. SALYER AND T. R. SWEET, *Anal. Chem.*, 30 (1958) 1632.

DETERMINATION OF TRACES OF FREE ACID
IN URANYL SALT SOLUTIONS

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(Received February 6th, 1963)

Various methods have been suggested to avoid interference of uranium(VI), which is caused by the hydrolysis of uranyl ion, in the titration of free acid in uranyl salt solutions. The method applied depends on the ratio of acid to uranium present. Direct alkalimetric titration may be used when the molar ratio of acid to uranium is about ten, the experimental error varying from 1-15%¹. Measurement of pH after partial neutralization with standard alkali is also possible^{2,3}, the acid content being found from curves for known uranyl nitrate concentrations. In other methods, the interference of uranium is eliminated by precipitation as peroxide or ferrocyanide⁴⁻⁶. Other widely used methods involve the inactivation of the hydrolyzable ion by complexing with oxalate⁷⁻⁹, fluoride^{5,10-12}, citrate¹³ or sulfate¹⁴; the neutralization point in the subsequent titration may be determined visually, potentiometrically¹¹ or conductometrically^{10,12}. However, these methods are empirical and the end-point is not distinct in the highly-buffered complexing medium. In order to avoid the use of complexing agents, an indirect cation-exchange method¹⁵ has been developed in which the total acidity, equivalent to both uranium and free acid, is determined after cation exchange; the amount of uranium is determined on a separate sample, and the acid equivalent to uranium is calculated and deducted from the total acidity, to yield the amount of free acid originally present.

No method, which is both simple and accurate, seems to be available in the literature for the determination of free acidity when the molar ratio of acid to uranium is low. In the present paper, a method which satisfies the above requirements is described. An aqueous solution of the sample is saturated with a neutral salt such as potassium nitrate or chloride. Most of the complexed uranium thus formed is then extracted by agitating with tri-*n*-butyl phosphate and, without separating the phases, the free acid is titrated potentiometrically to a fixed end-point.

EXPERIMENTAL

Reagents and apparatus

Reagent-grade tri-*n*-butyl phosphate (TBP) was freed from mono- and dibutyl phosphate by washing it twice with an equal volume of 0.1 *N* sodium hydroxide solution and three times with distilled water. The suspended water in the TBP was then removed by centrifugation. The main impurity in technical grade TBP was

butyl alcohol; this was removed by steam distillation from the TBP before washing. Uranyl nitrate hexahydrate (reagent grade) was used without further treatment or was recrystallized from a saturated solution at room temperature. All other reagents were of AnalaR quality. Titrations were carried out with model TTT 1 C automatic titrator (Radiometer, Copenhagen), using glass and calomel electrodes and a 6-ml microburette.

Procedure

Place 20 ml of TBP, 3 ml of water and 5–10 g of potassium nitrate or chloride in a 50-ml beaker. Agitate the mixture vigorously with a magnetic stirrer and adjust the pH to 3.0–3.2 with 0.1 *N* nitric acid. Stir the mixture further for 5 min and then slowly titrate with 0.1 *N* sodium hydroxide to pH 3.4. Then add an aliquot of the sample solution, containing not more than 1.0 millimole of uranium(VI) and not less than 0.1 millimole of free acid. Stir the mixture for a few minutes and titrate the free acid with 0.1 *N* sodium hydroxide to pH 3.4. Keep the aqueous phase saturated with excess of potassium nitrate and ensure that some solid salt is present throughout the titration.

RESULTS AND DISCUSSION

The optimum pH of the solution at the end-point of the titration and the most suitable neutral salt to employ were investigated. The accuracy of the method was then

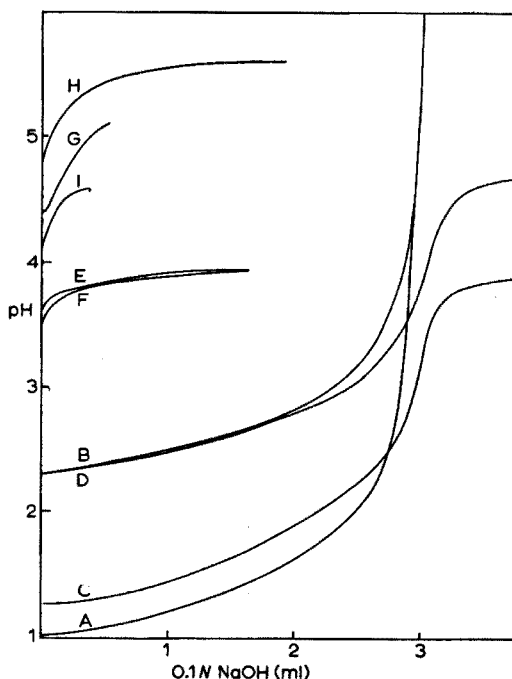


Fig. 1. Titration curves in 20 ml of TBP and 3 ml of water saturated with salts. a, KCl + HNO₃; b, KNO₃ + HNO₃; c, KCl + HNO₃ + UO₂²⁺; d, KNO₃ + HNO₃ + UO₂²⁺; e, KBr + UO₂²⁺; f, KCl + UO₂²⁺; g, NaNO₃ + UO₂²⁺; h, NH₄NO₃ + UO₂²⁺; i, KNO₃ + UO₂²⁺.

examined under these conditions, by applying various ratios of free acid to uranium.

A mixture of 20 ml of TBP, 0.3 millimoles of nitric acid and a saturated aqueous solution of potassium chloride or nitrate was titrated with 0.1 *N* alkali (curves a and b in Fig. 1). The sharp rise within the pH range 3–10 indicated that potassium chloride or nitrate had no buffer effect and did not interfere in the titration. These titrations were repeated in the presence of 0.8 millimoles of uranyl nitrate. As seen from curves c and d in Fig. 1, the rise in the pH near the neutralization point was less sharp in the presence of uranium. However, it was observed from these curves that within the pH ranges 2.6–3.6 and 3.3–4.4, in the case of potassium chloride and nitrate respectively, any pH value could be suitable to mark the end-point of the titration.

In order to find the optimum pH, a mixture of 20 ml of TBP and a saturated aqueous solution of the salt concerned was magnetically stirred and then 400 mg uranyl nitrate were added. The pH was then recorded at intervals while titrating with 0.1 *N* alkali. As indicated from curves e, f, g, h and i, at a given amount of uranium in the system, the curves for the nitrate mixture had a steeper slope than those for the chloride mixtures with correspondingly less hydrolysis of uranium during the titration. This was confirmed by the fact that the partition coefficient of uranium in the nitrate system was higher than that in the chloride system. (Table II, column 4).

If it is assumed that the uranyl nitrate hexahydrate used was acid-free*, the initial pH of the salt-saturated aqueous phase in the presence of uranium should be the required optimum pH for indicating the end-point of the titration. Although this initial pH in nitrate medium was around 4–5 (curves g, h and i), a lower value (pH 3.4) was arbitrarily chosen, in order to provide for a reasonable safety margin in case larger amounts of uranium might be present in the sample.

For the adjustment of the pH of the aqueous salt solution plus TBP before the introduction of the sample, it was found that equilibrium was more easily attained by back-titration than by direct acidification to pH 3.4.

In order to test the accuracy of the method, 0.1 *N* nitric acid was prepared and standardized as described in the procedure above, and in the presence of potassium nitrate plus TBP, without uranium. Within the range of 0.15–1.7 millimoles, the acid standardization figures varied by less than 0.13% from the arithmetic mean.

It was found experimentally that the minimum initial volume of the aqueous phase was about 3 ml. Excess of undissolved potassium nitrate was maintained throughout the titration in order to prevent the re-extraction of uranium from TBP during the titration. This may occur through dilution and lowering the concentration of nitrate by the titrant added.

When sodium nitrate was used as a salting-out agent, the pH adjustment was difficult, apparently because of slow equilibrium. Ammonium nitrate was unsuitable because of its excessive solubility in water.

A series of experiments was done in duplicate, taking known amounts of standard nitric acid in the presence of 0.8 millimoles of uranium. As shown in Table I, column 4, the relative error varied from 0.1–4% (the error was larger with very small titres in the last experiment). The accuracy of the method with varying concentrations of

* Uranyl nitrate hexahydrate recrystallized from aqueous solution at room temperature was used and the results obtained were identical to those described above.

TABLE I
TITRATION OF FREE ACID AT VARIOUS RATIOS OF H/U
(0.796 millimoles of uranyl nitrate, 20 ml of TBP and 3 ml of water)

<i>HNO₃</i> <i>taken</i> <i>(mmol)</i>	<i>Molar ratio</i> <i>of H/U</i> <i>in the system</i>	<i>HNO₃</i> <i>found</i> <i>(mmol)</i>	<i>Relative</i> <i>error</i> <i>(%)</i>	<i>Absolute</i> <i>titration</i> <i>error</i> <i>(ml 0.1 N NaOH)</i>	<i>Salt</i> <i>used</i> <i>(g)</i>
1.738	2.17	1.748	+ 0.6	0.11	15 KCl
0.734	0.92	0.735	+ 0.1	0.005	16 KCl
0.440	0.55	0.444	+ 0.9	0.035	5 KCl
0.147	0.18	0.148	+ 0.7	0.015	5 KCl
0.0740	0.09	0.0754	+ 1.9	0.013	5 KCl
0.0446	0.06	0.0486	+ 9.0	0.041	5 KCl
1.746	2.19	1.748	+ 0.1	0.02	15 KNO ₃
0.736	0.92	0.740	+ 0.5	0.04	8 KNO ₃
0.440	0.55	0.442	+ 0.4	0.02	5 KNO ₃
0.147	0.18	0.149	+ 1.4	0.02	5 KNO ₃
0.0734	0.09	0.0763	+ 3.9	0.03	5 KNO ₃
0.0440	0.06	0.0484	+ 10.0	0.04	5 KNO ₃

TABLE II
TITRATION OF FREE ACID IN THE PRESENCE OF VARIABLE AMOUNTS OF URANIUM

<i>Uranyl</i> <i>nitrate</i> <i>hexahydrate</i> <i>taken</i> <i>(total)</i> <i>(mmol)</i>	<i>Uranyl</i> <i>nitrate</i> <i>hexahydrate</i> <i>in aqueous</i> <i>phase</i> <i>after</i> <i>titration</i> <i>(mmol)</i>	<i>Molar</i> <i>ratio</i> <i>of H/U</i> <i>in the</i> <i>system</i>	<i>Distribution</i> <i>coefficient</i> <i>of uranium</i> <i>U in TBP/</i> <i>U in H₂O</i>	<i>HNO₃</i> <i>taken</i> <i>(mmol)</i>	<i>HNO₃</i> <i>found</i> <i>(mmol)</i>	<i>Relative</i> <i>error</i> <i>(%)</i>	<i>Salt</i> <i>used</i> <i>(g)</i>
0.2	0.010	1.53	7.7	0.289	0.290	+0.3	5 KCl
0.4	0.018	0.76	8.6	0.289	0.294	+1.7	5 KCl
0.8	0.030	0.38	9.8	0.289	0.294	+1.7	5 KCl
1.2	0.037	0.26	12.5	0.289	0.296	+2.4	5 KCl
1.6	0.044	0.19	14.0	0.289	0.301	+4.2	5 KCl
0.8	0.005	0.58	86	0.440	0.442	+0.4	5 KNO ₃

uranium is indicated in Table II. As much as 1 millimole of uranium could be tolerated in the titration of 0.1–0.2 millimoles of free acid. When the acid to uranium ratio was below 0.1, a large positive error was obtained. This was due to partial hydrolysis of unextracted uranium present in a relatively high concentration in the aqueous phase.

Since the titration is carried out without separation of the TBP, the applicability of this method for the direct analysis of acid when present in TBP is an obvious advantage.

SUMMARY

A method for the determination of free acid in the presence of uranium(VI) is suggested. It involves the extraction of uranium by TBP from a solution saturated with potassium nitrate or chloride in order to prevent interference from the hydrolysis of uranium. The end-point is detected potentiometrically at pH 3.4. The method is suitable for the determination of 0.1–1.5 millimoles of acid in the presence of as much as 1.0 millimole of uranium.

RÉSUMÉ

Une méthode de dosage d'acide libre, en présence d'uranium(VI), a été mise au point. Il s'agit d'extraction d'uranium par TBP d'une solution saturée avec nitrate de potassium pour éviter l'interférence par hydrolyse.

ZUSAMMENFASSUNG

Es wird eine Methode für die Titrierung von freier Säure unter Vorhanden sein von Uranium(VI) beschrieben. Uranium wird mit TBP aus einer mit Potassium-Nitrat gesättigten Lösung extrahiert, um den störenden Einfluss der Hydrolyse des Uraniums zu verhindern.

REFERENCES

- ¹ I. KOLTHOFF AND C. ROSENBLUM, *Acid-base Indicators*, Macmillan, New York, 1946.
- ² G. ALKIRE, *Anal. Chem.*, 24 (1952) 1228.
- ³ H. JONES, B. RIDER AND H. HENDRICKSON, The Determination of Free Acids in Solution of Aluminium, Thorium and Uranyl Nitrates, *U.S. At. Energy Comm. Report, KAPL-1497*, 1956.
- ⁴ C. RODDEN, *Analytical Chemistry of the Manhattan Project*, McGraw-Hill, New York, 1950, p. 214
- ⁵ R. MOORE AND A. SCHMIDT, The Determination of Free Acid in Solutions Containing Uranyl Nitrate, Aluminium Nitrate and Sodium Dichromate, *U.S. At. Energy Comm. Report, HW-14603*, 1957.
- ⁶ M. SMITH, The Determination of Free Acid in Plutonium Solutions, *U.S. At. Energy Comm. Report, LA-1864*, 1955.
- ⁷ G. BOOMAN, M. ELLIOT, R. KIMBALL, F. CARTAN AND J. REIN, *Anal. Chem.*, 30 (1958) 284.
- ⁸ R. A. SCHNEIDER AND M. J. RASMUSSEN, Oxalate-Complexing Alkalimetric Titration, *Analytical Technical Manual, HW-53368*, 1959 (Hanford Atomic Product Operation, General Electric).
- ⁹ Supplement No 3 to *Manual of the Analytical Methods Used by the Control Laboratory at the Chemical Processing Plant*, edited by J. H. SIKES AND J. E. REIN, IDO 14316, pp. 47, Oct. 1957 (Atomic Energy Division Phillips Petroleum Co., Idaho Falls, Idaho).
- ¹⁰ R. C. PROPST, *Conductometric Acidimetry in the Presence of Hydrolyzable Ions*, DP 76, NSA 10-1235 (1956) (Du Pont de Nemours, Savana River Lab.).
- ¹¹ O. MENIS, D. L. MANNING AND G. GOLDSTEIN, *Determination of Free Acid in Solutions of Uranyl Sulphate*, ORNL-2178, Nov. 8, 1956, NSA 11-929 (1957), Oak Ridge National Lab., Tenn.).
- ¹² L. PEPKOWITZ, W. SABAL AND D. DUTINA, *Anal. Chem.*, 24 (1952) 1956.
- ¹³ J. PFLUG AND F. MINER, *Anal. Chim. Acta*, 23 (1960) 362.
- ¹⁴ S. AHRLAND, *Acta Chem. Scand.*, 14 (1960) 2035.
- ¹⁵ Z. DIZDAR AND I. OBRENOVIC, *Anal. Chim. Acta*, 21 (1959) 560.

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM WITH
8-MERCAPTOQUINOLINE

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(Received February 22nd, 1963)

8-Mercaptoquinoline forms chelating compounds with a large number of cations; most of these complexes are coloured compounds, which are insoluble in water but soluble in a number of organic solvents. It has also been shown that these complexes are in general more stable than the corresponding salts of 8-hydroxyquinoline¹. The reagent has been used for the determination of vanadium² which forms a light-green precipitate of composition $\text{VO}(\text{C}_9\text{H}_6\text{NS})_2$ in weakly acid solution, and which is extractable into most organic solvents to give a yellow-green solution showing an absorption maximum at 412 $\text{m}\mu$. It has also been used for the determination of copper³ which forms a dark-brown precipitate, extractable by organic solvents.

8-Mercaptoquinoline has not, up to the present, been employed as a reagent for molybdenum. The present paper reports the investigations carried out and the procedure developed for the application of the reagent to the determination of molybdenum.

EXPERIMENTAL

Reagents

Standard molybdenum solution. This was prepared by dissolving 252.1 mg of sodium molybdate (A.R.) in 100 ml of water. The resulting solution contained 1 mg Mo/ml. From this solution, others containing differing amounts of molybdenum were prepared.

8-Mercaptoquinoline solution. The reagent was prepared as described by EDINGER⁴, with quinoline 8-sulphonic acid as starting material.

The solution used was obtained by dissolving 1 g of the compound in a mixture of 40 ml of concentrated hydrochloric acid and 60 ml of water. The solution, after being stirred for 10 min, was filtered, and the clear yellow filtrate was used in subsequent investigations.

Preliminary investigations

It was found that 8-mercaptoquinoline formed a yellow-brown complex with molybdenum which was extractable into organic solvents. The chloroform extract showed maximum absorbance at 425 $\text{m}\mu$ (Fig. 1). Formation of the molybdenum complex was highly dependent on pH; it was found that pH 1.3 gave the best results.

A plot of absorbance against pH for a solution containing 5 p.p.m. Mo is shown in Fig. 2.

The chloroform extract of molybdenum 8-mercaptoquinolate obeyed Beer's law up to 15 $\mu\text{g/ml}$. Above this concentration low results were obtained, probably because of an insufficiency of reagent; amounts larger than that suggested in the procedure given below were not examined.

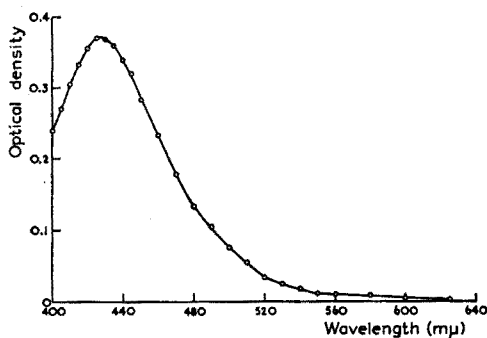


Fig. 1. Spectrum of the chloroform extract of molybdenum 8-mercaptoquinolate (5 $\mu\text{g Mo/ml}$).

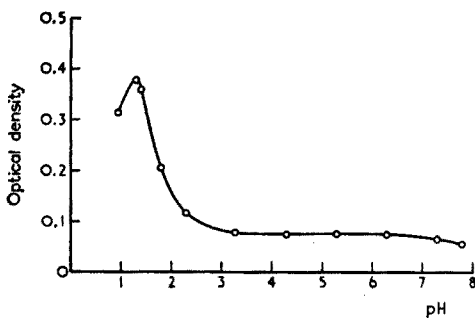


Fig. 2. Effect of pH on the absorbance of the complex (5 $\mu\text{g Mo/ml}$).

Procedure

In a separating funnel, place an aliquot (about 1 ml) of the molybdenum test solution. Add 10 ml of 2 *N* sodium acetate and 18 ml of 1 *N* hydrochloric acid, and mix well. Add 1 ml of the 8-mercaptoquinoline reagent and mix. After 2 min extract the yellow-brown colour or precipitate with 10 ml of chloroform. Shake for 2 min.

Allow the 2 phases to separate and filter the chloroform layer through cotton-wool into a 20-ml volumetric flask. Extract the aqueous layer with another 5 ml of chloroform and filter as before. Make up to the mark with chloroform. Carry a blank through the same operations. Measure the extinction of the molybdenum extract at 425 $m\mu$ against a blank and determine the amount of molybdenum from a calibration curve previously prepared from standard molybdenum solutions.

Results obtained for a number of molybdenum-containing solutions are shown in Table I.

TABLE I
DETERMINATION OF MOLYBDENUM WITH 8-MERCAPTOQUINOLINE

<i>Mo taken</i> (μg)	<i>Mo found</i> (μg)	<i>Error</i> (%)
150	149	-0.7
120	121	+0.8
100	100	0
80	79.8	-0.3
50	50	0

Interfering ions

The anions, acetate, phosphate, and cyanide do not interfere even if present in comparatively large amounts. Oxalate, citrate, and tartrate interfere seriously in the determination, probably because of the formation of molybdenum complexes which are stronger than that of molybdenum 8-mercaptoquinolate.

The cations mentioned in Table II form complexes with 8-mercaptoquinoline, but their interference is negligible under the conditions outlined above, and it is not necessary to complex them. Vanadium(V) interferes with the determination of molybdenum if present in amounts more than double that of molybdenum.

TABLE II
EFFECT OF DIVERSE CATIONS

<i>Mo taken</i> (μg)	<i>Diverse elements added</i> (μg)	<i>Mo found</i> (μg)	<i>Error</i> (%)
50	W(VI), 100	49	-2
50	V(V), 100	52.5	+45
50	As(V), 150	49.5	-1
50	Cr(III), 100	48.2	-3.6
100	U(VI), 100	99	-1
100	Cd(II), 1000	98	-2
100	Ni(II), 1000	98	-2
100	Co(II), 1000	102	+2
100	Fe(III), 1000	98.5	-3
100	Ag(I), 1000	98	-2
100	Hg(I,II) 1000	100	0

Some of the elements mentioned in Table II do not react with 8-mercaptoquinoline in highly acidic media, *e.g.* nickel(II) only forms a red complex in alkaline and neutral media. Others, such as tungsten and silver, are precipitated and cause little interference. The cations copper(II), bismuth(III), antimony(III) and zinc(II), however, interfere seriously with the determination of molybdenum and must, therefore, be removed. The following procedure was found to be successful.

To the molybdenum test solution containing one or more of the interfering ions, add 10 ml of 2 *N* sodium acetate and sufficient 5% sodium hydroxide to give a pH

of about 10 after the reagent has been added. Mix and leave for 2 min. Extract the 8-mercaptoquinolates of the interfering ions with chloroform, until the extract and the aqueous phase are both colourless. Add the required amount of 1 *N* hydrochloric acid, so that, after the addition of a further 2 ml of the reagent, the optimum pH for the molybdenum determination is obtained. Proceed in the recommended way for pure molybdenum solutions.

NOTES

(1) The above procedure depends on the fact that molybdenum does not react with 8-mercaptoquinoline in alkaline medium.

(2) If molybdenum has to be determined in solutions containing ions which require prior separation, it is recommended that the calibration curve should be prepared in the same way rather than from pure molybdenum standard solutions.

(3) The molar extinction coefficient of the molybdenum complex in chloroform is 8,000.

(4) Molybdenum is reduced to the quadrivalent state on reacting with the reagent.

(5) The composition of the molybdenum complex is $\text{Mo}(\text{C}_9\text{H}_8\text{NS})_2$.

SUMMARY

8-Mercaptoquinoline was found to be sensitive for the colorimetric determination of molybdenum. A procedure is outlined in which the complex formed, $\text{Mo}(\text{C}_9\text{H}_8\text{NS})_2$, is extracted into chloroform and the extinction measured at 425 μ . The effects and removal of interfering ions are discussed.

RÉSUMÉ

La mercapto-8-quinoléine est proposée comme réactif sensible pour le dosage colorimétrique du molybdène. Le complexe formé, $\text{Mo}(\text{C}_9\text{H}_8\text{NS})_2$, est extrait dans le chloroforme et l'extinction est mesurée à 425 μ . L'influence des ions gênants est examinée, ainsi que leur élimination.

ZUSAMMENFASSUNG

Als empfindliches Reagenz zur spektrophotometrischen Bestimmung von Molybdän wird 8-Mercaptochinolin empfohlen. Der gebildete Komplex, $\text{Mo}(\text{C}_9\text{H}_8\text{NS})_2$, wird mit Chloroform extrahiert und die Extinktion der Lösung bei 425 μ gemessen. Der Einfluss störender Fremdionen und deren Entfernung werden beschrieben.

REFERENCES

- ¹ YU. A. BANKOVSKII AND E. F. LOBANOVA, *Zh. Anal. Khim.*, 14 (5) (1959) 523.
- ² YU. A. BANKOVSKII, E. M. SHVARTS AND A. F. IEVINSH, *Izv. Akad. Nauk. Latv. SSR*, 1958, 121.
- ³ YU. A. BANKOVSKII AND A. F. IEVINSH, *Zh. Anal. Khim.*, 13 (6) (1958) 643.
- ⁴ A. EDINGER, *Ber.*, 41 (1908) 937.

STUDIES ON URONIC ACID MATERIALS

PART VIII¹. A COMPARATIVE STUDY OF SOME COLORIMETRIC METHODS OF ESTIMATING THE URONIC ACID CONTENTS OF POLYSACCHARIDES

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(Received January 20th, 1963)

Colorimetric methods are widely used in carbohydrate chemistry, being particularly useful for comparative analyses of large numbers of samples and for routine estimations of well-characterised materials.

Determination of the uronic acid content is a key analysis in studies of many carbohydrate materials, *e.g.* gums, mucilages, pectins, hemi-celluloses, mucopolysaccharides, glycoproteins and polysaccharides of marine origin. Such natural products are complex and often heterogeneous: they are usually closely associated with pigments, lipids, protein and inorganic materials. Elimination of these may not be possible without resultant degradation or modification (physical or chemical) of the carbohydrate material; careful choice of extraction conditions may be important².

Every carbohydrate material therefore presents a unique set of analytical requirements, and it is consequently difficult to formulate general analytical methods, particularly for colorimetric procedures. Methods developed and tested only with respect to synthetic mixtures of purified simple materials may give misleading results when applied to more complex natural materials. Colorimetric methods are susceptible to interferences by minor impurities, which need not be of natural origin. It is often difficult to remove *all* traces of the reagents added during purification stages; residual traces of inorganic ions can modify the chromophoric stages of reactions, causing inaccurate results.

For uronic acid determinations, the accepted reference procedures — which may themselves be subject to methodic errors — are (a) titration methods, which are not universally applicable, and (b) decarboxylation methods, which require up to 50 mg of material per determination in reactions of at least 2.5-h duration³⁻⁵. It is therefore not surprising that a large number of colorimetric methods, which are more rapid and require less material, have been proposed. These are based on non-stoichiometric reactions^{6,7}, and some of the reagents used are naphthoresorcinol⁸⁻¹⁰, phloroglucinol¹¹, thioglycolic acid¹², 2-thiobarbituric acid^{13,14}, 2-methyl-indole¹⁵, concentrated sulphuric acid¹⁶, alkaline hydroxylamine + iron (III)¹⁷, anthrone¹⁸⁻²⁰, carbazole²¹⁻²³ and carbazole + borate ions^{24,25}.

Conflicting reports regarding the specificity and validity of such colorimetric methods have been published^{8,9}. The non-specific nature of the anthrone reaction for uronic acid groups is well known, and the effect of nitrogenous materials on the

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reaction has been studied in a number of papers by HELBERT AND BROWN²⁰. The carbazole reaction²¹ has been reported^{26,27} to be unreliable in the presence of protein, but this was to be expected after DISCHE's initial report²¹ that proteins suppressed colour development, causing large errors. DISCHE further stated²¹ that the carbazole reaction "cannot be used for accurate determinations of absolute values for hexuronic acids in polysaccharides". In illustration of this, large discrepancies between colorimetric and decarboxylation values have been reported; for a seaweed polysaccharide, MCKINNEL AND PERCIVAL²⁸ found a uronic acid content of 18.3% (by decarboxylation) and 6.0% (by colorimetry)²², the desulphated material giving 23.5% (decarboxylation) and 10.2% (colorimetry).

To discover the extent of the variation in values given by different colorimetric methods, comparative studies have been made on a variety of carbohydrate materials; such a study does not appear to have been reported previously. Results given by the methods most frequently used for colorimetric estimations of uronic acids — the carbazole²¹, anthrone¹⁸, and hydroxamic acid¹⁷ methods — are presented and compared with the corresponding results obtained by decarboxylation⁵.

EXPERIMENTAL

Reference compounds

The samples of galacturonic acid monohydrate and glucuronolactone as standards were the specimens described in an earlier investigation². In addition to the analytical data already quoted², determinations of the neutralization equivalent gave values for the purity of the glucuronolactone and galacturonic acid of 97.2 and 96.0%, respectively.

The reference standard sample of galacturonic acid was used to make up the mixtures referred to in Tables I–III, and is listed as "Sample 1" in Table IV.

Acidic decarboxylation method

ANDERSON'S apparatus and reaction conditions⁴ were used. For this particular modification of LEFÈVRE AND TOLLEN'S³ reaction, a reaction time of 2.5 h has been confirmed⁵. In heterogeneous polysaccharides, pentoses and hexoses do not increase by more than 2–3% the yield of carbon dioxide from the uronic carboxyl groups⁴ (*cf.* TRACEY²⁹); amino sugars, peptides and proteins cause no interference³⁰.

Colorimetric methods

In all cases, absorption measurements were made against "blank" solutions prepared concurrently with the unknown sample.

(a) *Anthrone*. YEMM AND WILLIS' method¹⁸ was used, absorption being measured at 540 $m\mu$ after colour development for 15 min.

(b) *Carbazole*. DISCHE'S method²¹ was used, absorption in 10-mm silica cells being measured at 530 $m\mu$ after colour development for 2 h at 22°.

(c) *Alkaline hydroxylamine*. KAYE AND KENT'S procedure¹⁷ was followed in initial determinations, absorption being measured at 505 $m\mu$. The colour was observed to fade rapidly: a solution giving an optical density of 0.65 immediately after addition of iron(III) had later optical densities of 0.64 (10 min), 0.62 (20 min), 0.56 (30 min), 0.48 (40 min), 0.37 (50 min), and 0.25 (60 min).

KAYE AND KENT proposed¹⁷ that the absorption curve given by glucurone (line D,

Fig. 1) should be corrected by the amount of absorption given by glucose (line B, Fig. 1), so giving the "corrected glucurone" curve (line C). The uronic acids in natural polymeric materials are not, however, generally present as esters or lactones, and esterification must therefore be effected (methanolic hydrogen chloride, sealed

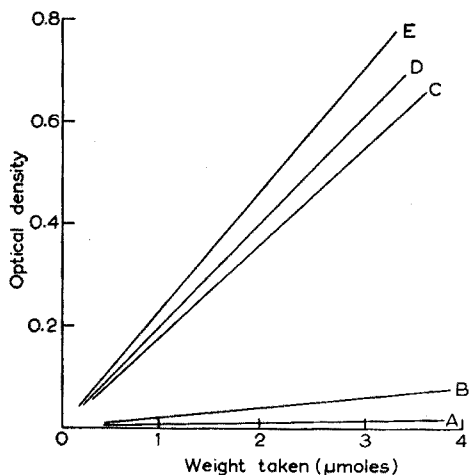


Fig. 1. Calibration curves for the alkaline hydroxylamine method. Curve (A) "esterified" hexoses and α -methyl hexoses, (B) glucose, (C) glucurone, corrected for glucose absorption, (D) glucurone, (E) "esterified" glucurone and galacturonic acid.

tube, 100°) before reaction with hydroxylamine. Hexoses thus treated gave line A in Fig. 1, whilst glucurone and galacturonic acid both gave line E. It is suggested that, if uronic acid X is to be estimated in a polymeric material, then the calibration curve should be obtained by subjecting pure X to the same analytical procedure as the polymer.

This method was found to be subject to four distinct modes of interference. (a) Some polysaccharides are not completely soluble in methanolic 1% hydrogen chloride, and incomplete esterification results. (b) Some esterified polysaccharides are not water-soluble, so that incomplete colour development is given. (c) Some polysaccharides give precipitates or gel formation on the addition of iron(III), so giving incomplete colour formation. (d) The presence of protein leads to high results. Materials subject to the interferences are correspondingly labelled A, B, C, or D in Table IV.

RESULTS

Interferences in the hydroxylamine method

The effect of protein on estimations by the hydroxylamine method is shown in Table I. Estimations were made on synthetic mixtures of edestin and galacturonic acid (reference standard sample).

The effect of hexoses and pentoses on estimations by the hydroxylamine method is shown in Table II. The use of galactose in place of glucose gave slightly greater positive errors; pentoses gave slightly smaller positive errors than glucose. The

TABLE I
EFFECT OF PROTEIN ON ESTIMATIONS

Composition of mixture		% Galacturonic acid indicated by the hydroxylamine method
% Protein	% Galacturonic acid	
17.7	82.3	88.7
50.3	49.7	130.5
90.6	9.4	190

TABLE II
EFFECT OF HEXOSES AND PENTOSE ON ESTIMATIONS

Composition of mixture		% Galacturonic acid indicated by the hydroxylamine method
% Glucose	% Galacturonic acid	
13.3	86.7	86.8
52.0	48.0	50.5
96.0	4.0	34.1

presence of hexoses and pentoses in a heterogeneous polysaccharide containing minor amounts of uronic acid may therefore lead to large errors in the colorimetric estimation of the uronic acid.

Interferences in the carbazole method

DISCHE²¹ found a 20% error with 0.1% protein in solution; colour suppression has been confirmed by recent investigations^{26,27}. DISCHE also reported²¹ that correction should be applied for the colour given by hexoses: the extent of the errors which can arise is shown in Table III.

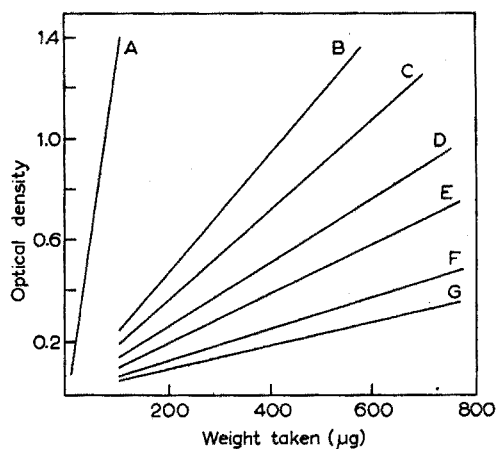


Fig. 2. Calibration curves for the anthrone method. Curve (A) pentoses, (B) glucose, (C) galacturonic acid, (D) galactose, (E) glucosamine hydrochloride, (F) glucuronic acid, (G) glucurono- δ -lactone.

TABLE III
ERRORS ARISING IN THE CARBAZOLE METHOD

Composition of mixture		% Galacturonic acid indicated by the carbazole method
% Glucose	% Galacturonic acid	
15.1	84.9	86.0
48.0	52.0	58.3
90.0	10.0	30.1

TABLE IV
COMPARISON OF RESULTS*

Sample	Uronic acid content (%) found by			
	Acidic decarboxy- lation	Hydroxyl- amine + iron(III)	Carbazole	Anthrone
1. Galacturonic acid, reference specimen	96.0	98.2	98.0	99.0
2. Galacturonic acid, specimen A	75.7	70.5	70.2	71.4
3. Galacturonic acid, specimen B	88.4	86.4	85.8	87.1
4. Galacturonic acid, specimen C	80.5	76.6	76.2	77.8
5. Trigalacturonic acid	92.4	87.9	87.5	88.0
6. Glucurone, specimen A	78.9	119.8	118.7	119.9
7. Glucurone, specimen B	90.9	117.2	116.6	117.3
8. Glucurone, specimen C	91.1	101.1	100.1	100.5
9. Glucurono- δ -lactone	9.9	51.7	51.4	62.1
10. Melezitose	1.6	14.8	15.0	17.0
11. Hyaluronic acid	31.6	42.2 (A,D)	34.8	57.6
12. Bone gelatin No. 112	2.3	12.2 (D)	12.3	27.6
13. Bone gelatin No. 188	3.5	14.0 (D)	—	—
14. Gum ghatti	14.6	8.5 (A)	—	—
15. <i>Combretum leonense</i> gum	20.0	15.8 (A,C)	—	—
16. Alginate acid	97.4	65.7 (A,C)	—	—
17. Seaweed polysaccharide	17.0	24.4 (A,B,D)	—	—
18. Ammonium pectate A	55.0	48.0 (A,C)	—	—
19. Ammonium pectate B	74.1	51.4 (A,C)	77.4	77.8
20. Pectin, 240 grade	57.9	42.5 (A,B)	60.2	67.8
21. Plant roots, specimen A	6.6	7.6	8.2	25.4
22. Plant roots, specimen B	7.1	8.3	9.7	27.6
23. Plant roots, specimen C	6.3	6.4	7.6	24.3
24. Plant roots, specimen D	7.2	6.8	8.0	24.2

(A) Polysaccharide incompletely soluble in methanolic 1% HCl.

(B) Esterified polysaccharide not water-soluble.

(C) Precipitation on addition of iron(III).

(D) Protein present.

Calibration curves

Calibration curves obtained for the reaction of some carbohydrate materials with anthrone are shown in Fig. 2. Different uronic acids give different absorptions. Interference by amino acids depends on the temperature, period of heating and acid

concentration²⁰; some amino acids enhance the colour, some have no effect, and some depress colour formation.

Comparison of results

Comparisons of the results obtained by the three colorimetric methods and by acidic decarboxylation are shown in Table IV. The origin of the samples was as follows: specimen 1 was the reference standard sample; specimen 2-4, 6-10, and 20 were commercial materials; 5 - given by Dr. W. W. REID (University of Bristol); 11 - prepared from umbilical cord by Dr. N. J. KING; 12 and 13 - given by Dr. G. STAINSBY, British Glue and Gelatin Research Association; 14 - *J. Chem. Soc.*, (1955) 1160; 15 - *Talanta*, 3 (1959) 118; 16 - *J. Chem. Soc.*, (1952) 1833; - 17 *J. Chem. Soc.*, (1959) 2168; 18 - *J. Chem. Soc.*, (1961) 5333; 19 - *J. Chem. Soc.*, (1958) 4020; 21-24 - oat rootlets grown for cell-wall studies, provided by Dr. W. M. CROOKE, Macaulay Institute, Aberdeen.

DISCUSSION

The results presented show that large relative errors may be given by the colorimetric methods studied; both high and low values may occur, and there appears to be little basis for prediction or correction of any bias. For those specimens giving high colorimetric values, the anthrone method consistently gave the highest results of all. The methods studied gave more self-consistent results for galacturonic acid specimens than for the samples of glucuronic acid investigated; the most satisfactory results were given for the specimen of highest purity, and this may have some significance. As has been pointed out recently³¹, colour reactions which give satisfactory estimations of pure substances, generally lack specificity when applied to biological specimens. In consequence, natural products containing small percentages of uronic acids cannot be analysed successfully by colorimetric methods: this has been found recently for mucopolysaccharides³² and for dextran products, on which colorimetry failed³³ at uronic acid/neutral sugar ratios of less than 1:10.

Uronic acid values obtained by colorimetric methods can clearly be subject to such large and unpredictable errors that it must be considered imprudent to place any reliance on values which cannot be substantiated (*cf.* ref. 34) by decarboxylation, which must be regarded as the best available reference method. It is not subject to interference from amino acids or amino sugars, and a correction can be applied for the carbon dioxide liberated from non-uronic acid residues if the sugar composition of the heterogeneous polysaccharide is known. Such amounts of carbon dioxide rarely contribute to the apparent uronic acid content by more than 2-3% absolute³⁰.

Colorimetry sometimes permits qualitative distinction to be made between uronic acids, and colorimetric results are most powerfully used in conjunction with decarboxylation data. Thus sodium heparinate gives substantially greater colorimetric absorptions than would be expected from its decarboxylation value, and this has led to speculation regarding the nature of the uronic acid present (*cf.* refs. 20, 24, 35). Similar deductions³⁶ from colorimetric results led to the identification of iduronic acid in chondroitin sulphate B, and may prove to be useful in investigations of the uronic acids present in alginic acid (*cf.* refs. 37, 38).

We thank Professor E. L. HIRST, C.B.E., F.R.S., for his interest in these studies,

and the Department of Scientific and Industrial Research for a maintenance grant (S.G.). We are grateful to Dr. W. W. REID, Dr. G. STAINSBY and Dr. W. M. CROOKE for providing specimens.

SUMMARY

Values for the uronic acid content of a variety of polysaccharide materials were obtained by colorimetric methods and by acidic decarboxylation; very large differences were found, particularly for heterogeneous biological materials. Colorimetric methods are useful for "screening" many samples rapidly, and for routine or comparative measurements on characterised products. For materials of unknown structure, however, colorimetric results should be interpreted with caution, especially when shortage of material does not permit corroborative decarboxylation or titration values to be obtained.

RÉSUMÉ

Les auteurs ont effectué une étude comparative sur la détermination de la teneur en "acide uronique" des polysaccharides; les valeurs obtenues à l'aide des méthodes colorimétriques sont très différentes de celles obtenues par décarboxylation, en particulier avec les substances biologiques hétérogènes. Les méthodes colorimétriques peuvent être utiles lors d'essais en série ou pour des mesures comparatives de produits connus. Pour les produits dont on ne connaît pas la structure, les résultats devraient être interprétés avec prudence.

ZUSAMMENFASSUNG

Bei der Bestimmung des Uronsäuregehaltes von Polysacchariden nach colorimetrischen Methoden und durch Decarboxylierungsreaktionen werden besonders bei heterogenem biologischen Material stark schwankende Werte erhalten. Colorimetrische Methoden eignen sich nur für Serienbestimmungen und Vergleichsmessungen bei gut charakterisierten Produkten. Bei Substanzen unbekannter Struktur sind colorimetrische Messwerte vorsichtig zu interpretieren, falls sie nicht durch eine Decarboxylierungsreaktion oder Titration gestützt werden können.

REFERENCES

- ¹ Part VII: D. M. W. ANDERSON AND D. GARBUTT, *J. Chem. Soc.*, in the press.
- ² D. M. W. ANDERSON, A. M. BEWS, S. GARBUTT AND N. J. KING, *J. Chem. Soc.*, (1961) 5230.
- ³ K. U. LEFÈVRE AND B. TOLLENS, *Ber.*, 40 (1907) 4513.
- ⁴ D. M. W. ANDERSON, *Talanta*, 2 (1959) 73.
- ⁵ D. M. W. ANDERSON AND S. GARBUTT, *Talanta*, 8 (1961) 605.
- ⁶ A. JENSEN, I. SUNDE AND A. HAUG, *Report No. 12, Norwegian Inst. for Seaweed Research, Trondheim*.
- ⁷ E. L. HIRST AND J. K. N. JONES, in PAECH AND TRACEY, *Modern Methods of Plant Analysis*, Vol. II, Springer-Verlag, Berlin, 1954, p. 275.
- ⁸ K. HEYNS AND C. KELCH, *Z. Anal. Chem.*, 139 (1953) 339.
- ⁹ A. GRAUER AND C. NEUBERG, *Anal. Chim. Acta*, 8 (1953) 422.
- ¹⁰ F. DICKENS AND D. H. WILLIAMSON, *Biochem. J.*, 68 (1958) 87.
- ¹¹ N. O. LINDH, *Arkiv Kemi*, 10 (1957) 569.
- ¹² Z. DISCHE, *J. Biol. Chem.*, 171 (1947) 725.
- ¹³ H. NEUKOM, *Chimia (Aarau)*, 14 (1960) 165.
- ¹⁴ R. ZIMMERMANN, W. BOCK AND K. TÄUFEL, *Z. Anal. Chem.*, 186 (1962) 350.
- ¹⁵ A. GRAUER, *Anal. Chim. Acta*, 8 (1953) 426.
- ¹⁶ I. H. BATH, *Analyst*, 83 (1958) 451.
- ¹⁷ M. A. G. KAYE AND P. W. KENT, *J. Chem. Soc.*, (1953) 79.
- ¹⁸ E. W. YEMM AND A. J. WILLIS, *Biochem. J.*, 57 (1954) 508.
- ¹⁹ H. NEUKOM AND P. HUI, *Chimia (Aarau)*, 13 (1959) 330.
- ²⁰ J. R. HELBERT AND K. D. BROWN, *Anal. Chem.*, 33 (1961) 1610; 31 (1959) 1700; 28 (1957) 1464.
- ²¹ Z. DISCHE, *J. Biol. Chem.*, 167 (1947) 189; 183 (1950) 489.
- ²² E. A. MCCOMB AND R. M. MCCREADY, *Anal. Chem.*, 24 (1952) 1630 and 1986.
- ²³ J. M. BOWNESS, *Biochem. J.*, 70 (1958) 107.
- ²⁴ J. D. GREGORY, *Arch. Biochem. Biophys.*, 89 (1960) 157.
- ²⁵ T. BITTER AND R. EWINS, *Proc. Biochem. Soc.*, 81 (1961) 43P.
- ²⁶ P. A. ANASTASSIADIS AND R. H. COMMON, *Can. J. Biochem. Physiol.*, 36 (1958) 413.
- ²⁷ A. A. LEACH, *J. Appl. Chem. (London)*, 11 (1961) 10.

- ²⁸ J. P. MCKINNELL AND E. PERCIVAL, *J. Chem. Soc.*, (1962) 3141.
²⁹ M. V. TRACEY, *Biochem. J.*, 43 (1948) 185.
³⁰ S. GARBUTT, *Ph.D. Thesis*, University of Edinburgh, 1960.
³¹ G. W. OERTEL AND E. KAISER, *Clin. Chim. Acta*, 7 (1962) 700.
³² S. B. KADKOL AND H. S. R. DESIKACHAR, *Current Sci. (India)*, 30 (1961) 337.
³³ W. J. WHELAN, personal communication.
³⁴ M. M. RAPPORT, K. MEYER AND A. LINKER, *J. Am. Chem. Soc.*, 73 (1951) 2416.
³⁵ Z. DISCHE AND K. MEYER, *Federation Proc.*, 6 (1947) 248.
³⁶ P. HOFFMAN, A. LINKER AND K. MEYER, *Science*, 124 (1956) 1252.
³⁷ F. G. FISCHER AND H. DÖRFEL, *Z. Physiol. Chem.*, 301 (1955) 224; 302 (1955) 186.
³⁸ D. W. DRUMMOND, E. L. HIRST AND E. PERCIVAL, *J. Chem. Soc.*, (1962) 1208.

Anal. Chim. Acta, 29 (1963) 31-38

STUDIES ON URONIC ACID MATERIALS

PART IX¹. THE SIMULTANEOUS DETERMINATION OF
URONIC ACID AND ALKOXYL GROUPS IN
POLYSACCHARIDES BY REFLUX WITH HYDRIODIC ACID

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(Received February 27th, 1963)

Although colorimetric methods of estimating uronic acid groups are useful under certain conditions¹, they do not give absolute values and are subject to interferences when determinations on heterogeneous materials are required; particularly serious errors can arise when proteinaceous matter is present¹. The random and individual nature of the interferences makes it difficult for their effect to be predicted and for suitable corrections to be applied.

Acidic decarboxylation is therefore much preferred analytically², since the side-reactions given by uronic materials, and the liberation of carbon dioxide from non-uronic residues, lead to comparatively small errors. These rarely exceed 3% absolute, and are always positive; their probable extent can be calculated once the proximate composition of the polysaccharide is known. In particular, interference from proteinaceous matter is negligible.

The kinetics and mechanism of the acidic decarboxylation of uronic acids have been investigated³. Although the analytical reaction⁴ based on reflux with 19% (w/w) hydrochloric acid for 2.5 h⁵ has given satisfactory results for several years, it became apparent that the following modifications would improve the method: (a) reduction of the required reaction time (b) increase in the specificity and sensitivity of determining the carbon dioxide evolved, and (c) development of apparatus simpler than that previously described⁴, preferably eliminating specialised glass-blowing (this suggestion was made by workers in several other laboratories).

This paper describes how each of these advantages has been achieved. The modification involve (a) the use of constant-boiling hydriodic acid (55% w/w) as the decarboxylating medium, (b) the use of vapour-phase infra-red determination⁶ of the carbon dioxide evolved, and (c) the use of a combined reaction-flask and reflux condenser (commercially available) as the reaction vessel. The assembled apparatus is therefore identical to that already described⁷ for alkoxy determination, and it is possible to determine the alkoxy and uronic content of a sample simultaneously.

This analytical method combines parts of the procedures of two earlier workers. BUSTON⁸ used a modified Zeisel apparatus for uronic acid determinations with hydrochloric acid, and VOLLMERT⁹ used hydriodic acid (57%) as the decarboxylating

medium. VOLLMERT recommended a reaction period of "1-2 h"; our experiments with characterised reference materials have shown that constant-boiling hydriodic acid gives complete decarboxylation in 1.5 h.

EXPERIMENTAL

Apparatus

The combined reaction flask and condenser [B.S. 1428: part C1: 9154 (part 2 apparatus)], delivery tube, and vapour trap have been described⁷. The apparatus is assembled as shown in ref. 7, Fig. 1, except that soda asbestos and Anhydrone are not added to the delivery tube. The omission of Anhydrone was found to give more complete and more reproducible recoveries of carbon dioxide: the traces of water vapour collected and subsequently transferred to the gas-cell do not interfere with the spectroscopic determinations required and do not cause significant "fogging" of the cell windows. Nitrogen (6-8 ml per min) is used as flow-gas; the methods of pretreatment and of stabilising the flow-rate have been described⁷.

Spectroscopic determination of carbon dioxide and alkyl iodides

The collection of reaction products, and their quantitative transfer to a gas-cell¹⁰ for determination, have been described previously⁸ as have all the aspects of the determination of alkoxy groups by this method¹¹.

Construction of calibration curves for carbon dioxide

Calibration is based on the very strong absorption by carbon dioxide at 2350 cm^{-1} ; very few other gases give absorption in this part of the spectrum. Calibrations can be achieved manometrically⁶, or by collecting the carbon dioxide given by known weights of sodium carbonate (M.A.R.) when reacted with acid in the decarboxylation apparatus. Fig. 1 shows a calibration curve obtained in this way, together with the calibration curve, for the same cell, for methyl iodide. After the known weight of carbon dioxide has been transferred to the gas-cell, dry air should be admitted so that the cell contents are at atmospheric pressure⁶. This minimises pressure broadening effects, and the trace amount of carbon dioxide so introduced is compensated by the double-beam operation of the spectrometer.

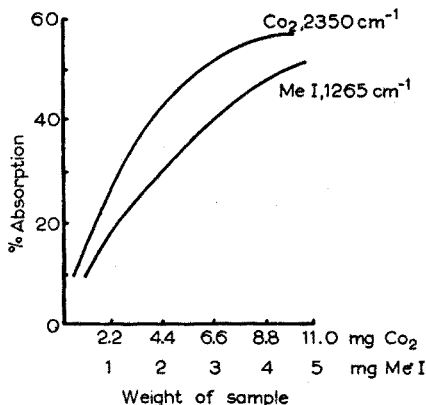


Fig. 1. Calibration curves for carbon dioxide (at 2350 cm^{-1}) and methyl iodide (at 1265 cm^{-1}). Length of gas-cell = 12.5 cm, volume = 56 ml.

Reagents and compounds

Analar hydriodic acid (about 55%, B.D.H. Ltd.) gives satisfactory results. Batches (250 ml) of the acid are preconditioned⁷ before use by refluxing, with continuous passage of nitrogen at 6–8 ml per min, for 1 h.

The standard samples of glucurone, galacturonic acid, and alginic acid have been described¹². The origin of other specimens is shown in footnotes to the Tables.

Procedure

The weight of sample taken should be sufficient to give a yield of carbon dioxide which falls within the range of sensitive response for the calibrated gas-cell: with the cell normally used (length 12.5 cm; internal volume = 56 ml) in our experiments, the suitable range of carbon dioxide is 1–6 mg. (Gas-cells giving similar sensitivities can be used with the less expensive bench-type spectrometers now available.)

The sample is refluxed for 1.5 h with 6 ml of the hydriodic acid. Some materials may be added to the reaction flask in a suitable long-handled weighing- spoon, but this is not possible with bulky, freeze-dried specimens, or with materials (*e.g.* gums, pectins) which “cake” or gel on the addition of aqueous solutions. The following technique is therefore recommended for all samples. The sample is weighed in a small weighing tube, in which dissolution is achieved by the addition of hydriodic acid (2 ml). The solution (or suspension in atypical cases) is transferred quantitatively to the reaction flask with the aid of a further four 1 ml portions of hydriodic acid.

Aqueous solutions may be analysed as follows. The concentration of the solution is adjusted so that 1 ml will yield a suitable weight of carbon dioxide. A 1-ml aliquot is transferred to the reaction flask, and then just under 5 ml of hydriodic acid (*s. g.* 1.94; about 66%) is added. The final volume is therefore approximately 6 ml and the acid is virtually of azeotropic composition. This procedure often eliminates drying stages if the isolation of solid material (*e.g.* in intermediate stages of a process) is not otherwise required.

RESULTS

Determination of the reaction-time required for quantitative results

Kinetic experiments with well-characterised samples¹² of glucurone, galacturonic acid and alginic acid showed that reflux for 1.5 h gave quantitative decarboxylation. Reflux for longer periods gave very little “over-production” of carbon dioxide, in marked contrast to previous experiences⁴ with hydrochloric acid. Table I shows the agreement given by the hydrochloric and hydriodic acid reactions.

The “apparent uronic content” given by non-uronic compounds

All carbohydrates suffer some decomposition when refluxed with strong mineral acids, the carbon dioxide evolved indicating an apparent uronic acid content. In typical heterogeneous materials containing, say, 20% uronic acid + 30% hexose + 50% pentose, decomposition of the pentose and hexose will increase the yield of carbon dioxide originating from decarboxylation of the uronic residues. It is important to know the extent to which this occurs. The effect was investigated fully¹³ for the hydrochloric acid reaction, and some of the values obtained are compared in Table II with the corresponding values given by reflux for 1.5 h in 55% hydriodic acid (*cf.* ref. 14, 15).

TABLE I
THE URONIC ACID CONTENT (%) OF SOME MATERIALS

Specimen	By decarboxylation with hydriodic acid (55%) for 1.5 h	By decarboxylation with hydrochloric acid (19%) for 2.5 h
Glucurone ^a	96.7	97.2
Galacturonic acid ^a	97.2	96.0
Alginate acid ^a	96.6	97.1
Acacia senegal gum ^b	16.1	15.9
Acacia seyal gum (Sample VIII) ^c	12.0	11.9, 11.6
Pectic acid ^b	62.8	61.8

^a See ref. 12.

^b Bulk commercial samples.

^c ANDERSON AND HERBICH, *J. Chem. Soc.*, (1963) 1.

TABLE II
THE "APPARENT URONIC ACID" CONTENT OF SOME NON-URONIC MATERIALS*

Specimen	Apparent uronic acid content from	
	Reflux with 19% HCl for 2.5 h	Reflux with 55% HI for 1.5 h
Melezitose	1.6	1.8
Sucrose	2.6	3.2
Lactose	1.7	2.0
Glucoheptose	4.2	3.2
Mannose	3.5	3.4
Glucose	2.0	2.8
Galactose	2.8	2.5
Xylose	1.9	2.4
Arabinose	2.1	2.9
Ribose	2.2	3.4
Rhamnose	3.5	3.1
Fucose	3.0	2.2
Erythrose	4.8	3.2
Erythritol	0.1	0.4
2-Deoxy-glucose	1.2	2.4
Potato starch	—	2.5
Glycogen	—	3.1
Agar	—	6.4
Carrageenan	—	3.7
Inulin	3.0	3.1
Glucosamine hydrochloride	0.3	1.0
Bone gelatin No. 112*	2.3	1.7
No. 188*	3.5	3.5
Edestin	—	0.4
1, 5-Gluconolactone	9.9	14.8
Ascorbic acid	99.4	99.2

* All samples were of commercial origin, except those marked* (research specimens from B.G.G.R.A.).

Identification of other volatile reaction products

The volatile reaction products evolved in reflux periods of up to 24 h were investigated for reactions in 19% hydrochloric acid and 55% hydriodic acid. With both these mineral acids, hexuronic acids and pentoses gave small amounts of furan, acetone and acetaldehyde; hexoses and methyl pentoses gave some 2,5-dimethylfuran and some 2-methylfuran, respectively. As indicated in Table III, however, the relative yields of these products were dependent on the mineral acid used.

TABLE III
THE VOLATILE PRODUCTS GIVEN BY SOME CARBOHYDRATES*

Compound	Period of reflux (h)	Volatile products from reflux with 19% HCl				Volatile products from reflux with 55% HI			
		Carbon dioxide	Furan	Acetaldehyde	Acetone	Carbon dioxide	Furan	Acetaldehyde	Acetone
Glucurone	0-3	+++	++	—	+	+++	tr	—	++
	3-9	+	tr	tr	tr	+	—	—	+
	9-12	+	+	+	+	tr	—	+	—
	12-24	tr	+	++	tr	tr	—	+	—
Galacturonic acid	0-6	+++	++	—	+	+++	tr	—	++
	6-9	+	+	tr	+	+	—	tr	tr
	9-12	+	+	+	tr	tr	—	tr	—
	12-24	tr	tr	tr	tr	tr	—	tr	—
Arabinose	0-12	+	++	—	—	+	++	tr	+
	12-24	+	++	+	—	tr	—	—	—
Ribose	0-24	+	+	+	—	+	—	tr	++

* +++ large amount, ++ small amount, + minor amount, tr just detectable.

The simultaneous determination of uronic and methoxyl contents

In spectroscopy, the most reliable results are generally obtained from absorptions of 30-70%. Under the conditions described, however, absorption at 2350 cm^{-1} is most sensitive to change in concentration for small amounts of carbon dioxide, *i.e.* those giving 15-50% absorption. As shown in Fig. 1, the gas-cell gives its most sensitive response for 1-6 mg quantities of carbon dioxide. The range of sample weights required is therefore: 4-24 mg for pure uronic acids or polyuronides, and 20-120 mg for materials containing 20% uronic acid.

This gas-cell also gives a sensitive response to 1-4 mg methyl iodide; nominal 50-mg samples therefore allow accurate simultaneous determinations of uronic acid and methoxyl contents in the range 8-48% and 0.5-2%, respectively. Methoxyl contents outwith this range can be determined by transferring the cell contents to a more sensitive or less sensitive gas-cell, as necessary. Simple procedures facilitating quantitative recovery from gas-cell to cold trap for transfer to a different cell have been described⁶. Although reflux periods in excess of 1 h during Zeisel determinations on carbohydrates can lead to error if a volumetric finish is used¹⁰, longer reflux periods are not detrimental when the specific spectroscopic method is used to determine alkyl halides collected in a cold trap.

DISCUSSION

The amounts of carbon dioxide evolved from non-uronic materials in this rapid hydriodic acid reaction differ slightly from the amounts released by hydrochloric acid: on balance, however, results by either method are unlikely to be high by more than 3% absolute, even if nitrogenous materials are present.

The relative yields of other volatile products also differ from those evolved in hydrochloric acid decarboxylation.

This does not influence the analytical determination of carbon dioxide, but indicates that slight changes occur in the mechanism of the decomposition stages which follow the decarboxylation step. In particular, decarboxylation with hydriodic acid produces larger quantities of acetone (*cf.* ref. 17, 18).

The ability to determine alkoxy and uronic groups simultaneously in a 1.5-h reaction is of value in routine determinations (economy of time) and in research investigations (economy of material). The method is particularly useful for determinations on pectins (50–70% uronic acids, 1–5% methoxyl) and plant gums (5–50% uronic acid, 0–2% methoxyl). Methoxyl contents of 1% are of structural significance¹⁹; recent studies on a number of *Acacia* gums have shown the presence of methoxyl groups, of which earlier investigators, particularly those dealing with gum arabic (*Acacia senegal*), appear to have been unaware.

A further advantage of the present method is its ability to differentiate between methoxyl and ethoxyl groups⁷. This is useful in investigations of artefacts arising from solvent retention^{20,21} or from attempted reductions with potassium borohydride or diborane.

For complex multi-stage reactions, spectroscopic determination of carbon dioxide has considerable advantages over the conventional chemical method. The spectroscopic method is specific and sensitive. Errors caused by the evolution of other acidic products are eliminated; the possibility of traces of the decarboxylating acid being carried over by the flow-gas is no longer an inherent source of high results. Other investigators have recently discussed the limitations of conventional methods of determining carbon dioxide in reactions which release other acidic vapours; as a result, the use of non-aqueous solvents²², carbonic anhydrase²³, gas chromatography²⁴ and infra-red absorption^{25–27} have all been recommended. Non-aqueous solvent methods may require purification of the carbon dioxide before its absorption²⁸.

The sensitivity of the present method may be increased by the use of more sensitive gas-cells^{10,29}, but the following simple technique is of value when a determination is required on an inadequate amount of sample which, by itself, would give an infra-red absorption (say < 15% absorption) too small for accurate measurement. The weighed sample is pre-dissolved in the usual way and added to the reaction flask, to which had been added a known weight (sufficient to give 20–30% absorption) of the carbonate used in constructing the calibration curve. The weight of carbon dioxide from the polysaccharide is obtained as the difference between the weight recovered and the weight expected from the amount of carbonate taken.

We thank Professor E. L. HIRST, C.B.E., F.R.S., for his interest in these methods, the British Glue and Gelatin Research Association for gifts of standard gelatin samples, the Department of Scientific and Industrial Research for a maintenance grant (to S.G.), and the P.C.S.I.R., Karachi, for granting study leave and financial support (to S.S.H.Z.).

SUMMARY

A reaction period of 2.5 h is required for the decarboxylation of uronic acid groups with 19% (w/w) hydrochloric acid, but 55% (w/w) hydriodic acid gives complete decarboxylation in 1.5 h. This rapid reaction can be carried out in a standard Zeisel reaction flask and condenser. Vapour phase infra-red spectroscopy gives a specific determination of the carbon dioxide evolved, and facilitates simultaneous determinations of any alkoxyl groups present. The proposed method is particularly useful for pectins and plant gums; it gives greater sensitivity and reproducibility than previous methods.

RÉSUMÉ

La durée de décarboxylation de groupes uroniques peut être considérablement réduite, en utilisant l'acide iodhydrique à 55%, à la place de l'acide chlorhydrique à 19% (1 h. 30, au lieu de 2 h. 30). La spectroscopie infra-rouge en phase gazeuse permet de doser l'anhydride carbonique dégagé et facilite des déterminations simultanées de n'importe quel groupe alcoyle présent. La méthode proposée est particulièrement utile pour les pectines et gommages végétales. Elle permet d'obtenir une sensibilité et une reproductibilité supérieures à celles des autres méthodes.

ZUSAMMENFASSUNG

Die Geschwindigkeit der Decarboxylierungsreaktion von Uronsäuren kann durch Verwendung von 55%iger Jodwasserstoffsäure an Stelle von 19%iger Salzsäure beträchtlich erhöht werden. Das gebildete Kohlendioxyd wird IR-spektroskopisch bestimmt, wobei gleichzeitig die Bestimmung etwa vorhandener Alkoxygruppen möglich ist. Die beschriebene Methode eignet sich besonders zur Untersuchungen von Pektinen und Pflanzengummi. Die Empfindlichkeit und Reproduzierbarkeit ist grösser als bei den älteren Methoden.

REFERENCES

- 1 Part VIII: D. M. W. ANDERSON AND S. GARBUTT, *Anal. Chim. Acta*, ACA 3096.
- 2 D. M. W. ANDERSON, S. GARBUTT AND J. F. SMITH, *Talanta*, 9 (1962) 689.
- 3 D. M. W. ANDERSON AND S. GARBUTT, *J. Chem. Soc.*, (1963) 3204.
- 4 D. M. W. ANDERSON, *Talanta*, 2 (1959) 73.
- 5 D. M. W. ANDERSON AND S. GARBUTT, *Talanta*, 8 (1961) 605.
- 6 D. M. W. ANDERSON, *Analyst*, 84 (1959) 50.
- 7 D. M. W. ANDERSON AND J. L. DUNCAN, *Talanta*, 7 (1960) 70.
- 8 H. W. BUSTON, *Analyst*, 57 (1932) 220.
- 9 B. VOLLMERT, *Makromol. Chem.*, 3 (1949) 140.
- 10 D. M. W. ANDERSON AND J. L. DUNCAN, *Chem. & Ind. (London)*, 1662 (1958).
- 11 D. M. W. ANDERSON AND J. L. DUNCAN, *Talanta*, 8 (1961) 1.
- 12 D. M. W. ANDERSON, A. M. BEWS, S. GARBUTT AND N. J. KING, *J. Chem. Soc.*, (1961) 5230.
- 13 S. GARBUTT, *Ph. D. Thesis*, University of Edinburgh, 1960.
- 14 A. G. NORMAN, *Nature*, 143 (1939) 284.
- 15 M. V. TRACEY, *Biochem. J.*, 43 (1948) 185.
- 16 D. M. W. ANDERSON AND J. L. DUNCAN, *Talanta*, 8 (1961) 241.
- 17 C. R. MARSHALL AND F. W. NORRIS, *Biochem. J.*, 31 (1937) 1296.
- 18 P. K. SAHA, A. K. MAZUMDAR AND P. B. SARKAR, *Textile Res. J.*, 27 (1957) 85.
- 19 G. O. ASPINALL, E. L. HIRST AND N. K. MATHESON, *J. Chem. Soc.*, (1956) 989.
- 20 D. W. DRUMMOND AND E. E. PERCIVAL, *J. Chem. Soc.*, (1961) 3908.
- 21 D. M. W. ANDERSON AND N. J. KING, *Talanta*, 8 (1961) 497.
- 22 A. PATCHORNIK AND Y. SHALITIN, *Anal. Chem.*, 33 (1961) 1887.
- 23 A. L. UNDERWOOD, *Anal. Chem.*, 33 (1961) 955.
- 24 P. G. JEFFERY AND P. J. KIPPING, *Analyst*, 87 (1962) 379.
- 25 J. A. KUCK, J. W. BERRY, A. J. ANDREATCH AND P. A. LENTZ, *Anal. Chem.*, 34 (1962) 403.
- 26 H. POBINER, *Anal. Chem.*, 34 (1962) 878.
- 27 H. A. C. MONTGOMERY AND N. S. THOM, *Analyst*, 87 (1962) 689.
- 28 J. A. GRANT, J. A. HUNTER AND W. H. S. MASSIE, *Analyst*, 88 (1963) 134.
- 29 D. M. W. ANDERSON, *Talanta*, 8 (1961) 832.

KINETICS OF THE EXTRACTION OF CHROMIUM(III) INTO CHLOROFORM
CONTAINING ACETYLACETONE

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(Received January 3rd, 1963)

In recent years the solvent extraction of metal ions from an aqueous phase into an immiscible organic phase containing a chelating reagent has attracted wide attention. Numerous studies have appeared in the literature that relate the distribution of the metal ion between the two phases to the equilibrium pH of the aqueous phase, the equilibrium concentration of the chelating reagent in the organic phase, and the equilibrium constants of the various reactions participating in the extraction process. Such studies generally assume that equilibrium among all species present in the extraction system has been attained. A survey of the literature indicates that little attention has been given to the study of solvent extractions under non-equilibrium conditions. Investigations of the rates of extraction of metal ions with dithizone have been reported by WALKLEY¹, IRVING, ANDREW AND RISDON², GEIGER³, and HONAKER AND FREISER⁴. SCHWEITZER AND RIMSTIDT⁵ have reported on the rate of solvent extraction of some zinc β -diketone chelates. RUBIN AND HICKS⁶ studied the kinetics of the extraction of plutonium into benzene containing thenoyltrifluoroacetone, and TAFT AND COOK⁷ have investigated the rate of reaction of various metal ions with thenoyltrifluoroacetone. In addition to these studies there are some qualitative observations scattered throughout the literature. In several instances the presence of very strong complexing agents in the aqueous phase has been observed to reduce extraction rates⁸.

It has been known for some time that most rates of substitution in chromium(III) complexes in aqueous solution are quite slow. A survey of earlier studies is given by TAUBE⁹, and later additions are given by BASOLO AND PEARSON¹⁰. The peculiarly slow behavior of chromium(III) toward solvent extraction with acetylacetonone was recently noted by MCKAVENEY AND FREISER¹¹. These investigators reported no extraction of chromium(III) from a sulfate medium into a 1:1 chloroform-acetylacetonone mixture in the pH range from 0.0 to 6.0 after shaking both phases for 30 min. This failure to extract was attributed to the extremely slow rate of formation of the metal chelate. This slow rate has been employed to effect separations of chromium from aluminum, iron, vanadium, molybdenum, and titanium¹¹. MORRISON AND FREISER¹² recommend a refluxing of the aqueous chromium solution with acetylacetonone at pH 6.0 for 1 h in order to bring about complete extraction.

This investigation is an attempt to study in more detail the extraction kinetics of chromium(III) from an aqueous phase into a chloroform phase containing acetylacetone.

EXPERIMENTAL

Apparatus and reagents

Extractions were performed by agitating the samples in 25-ml glass-stoppered Erlenmeyer flasks with Teflon-coated stirring bars on a multiple stirring assembly. The flasks were partially submerged in water which was circulated through an aluminum tray above the stirring assembly. The water temperature was maintained at $30.0 \pm 0.5^\circ$. All pH measurements were made with a Beckman 39183 Combination Electrode and a Beckman Zeromatic pH Meter. This meter was standardized against Beckman buffer solutions of pH values 4.02 and 7.02 at 30.0° . Measurements of radioactivity were performed with a Tracerlab P-20DW Well Scintillation Detector connected to a Versa-Matic II Scaler.

The water used to prepare solutions was distilled and then further purified by passing it through a column containing Amberlite MB-3 mixed bed resin. All chemicals were reagent grade except the acetylacetone (2,4-pentanedione) which was purified by fractional distillation. The fraction boiling from 135 to 137° (750 mm Hg) was used. Chromium-51 was obtained from Oak Ridge National Laboratory in 1.0 *N* hydrochloric acid.

Procedures

The chromium-51 obtained from Oak Ridge was converted to chromium(III) perchlorate by evaporating to dryness an aliquot of the diluted stock solution with 1-ml portions of concentrated perchloric acid repeatedly. The resulting chromium(III) perchlorate solution was diluted with 1 *N* perchloric acid to give a chromium concentration of $10^{-2.7}$ *M*.

Samples consisting of 10 ml of chloroform-saturated water, 0.1 *M* in sodium perchlorate, and 10 ml of water-saturated chloroform, 0.1, 0.3, 1.0, or 3.0 *M* in acetylacetone, were equilibrated at 30.0° at a predetermined constantly-maintained pH value for at least an hour. Preliminary studies had shown that after this time equilibrium of the partitioning acetylacetone between the two phases was reached. Then 50 μ l of the radioactive chromium perchlorate was introduced to give an aqueous chromium concentration of about $10^{-5.0}$ *M*. For higher chromium concentrations aliquots of a $10^{-2.0}$ *M* solution of non-radioactive chromium(III) perchlorate were refluxed with 50 μ l of the radiolabelled chromium(III) perchlorate on a steam bath for 24 h and the combined solution was added to the extraction system.

After addition of the metal ion, the pH was rapidly readjusted to the predetermined value by the addition of 1 *M* sodium hydroxide solution. Samples of 100 μ l were taken from each phase at several time intervals after stopping the stirrer and allowing the extraction flasks to stand for 1 to 5 min to ensure separation of the layers. These samples were placed in small vials containing 2 ml of water or chloroform and were counted on the well-type scintillation counter.

The organic phases containing the chromium(III) chelate after extraction from the aqueous phase were collected and separated from remaining water. Portions (10 ml) of these chloroform solutions were used with 10 ml of chloroform-saturated water

containing 0.1 *M* sodium perchlorate, 1.0 *M* perchloric acid, 0.1 *M* ethylenediaminetetraacetic acid, or 0.1 *M* sodium hydroxide to study the rates of back-extractions of the chromium(III) into these media.

In order to compare the rates of extraction of the aquated chromium(III) with those of the chloro-complex, an aliquot of the original radioactive solution was refluxed with 1 *N* hydrochloric acid for 24 h. An aliquot (50 μ l) of this solution was added to 10 ml of chloroform-saturated water, 0.1 *M* in sodium chloride, which was in contact with 10 ml of water-saturated chloroform, 1.0 *M* in acetylacetone, the two phases having been pre-equilibrated for at least 1 h at a predetermined pH value. The extraction was then followed as described previously.

To study the effects of changing the oxidation state of chromium(III) prior to the extraction, the chromium(III) was reduced by passage through a conventional micro Jones reductor. The resulting solution was eluted from the column with a 10-ml portion of chloroform-saturated water, 0.1 *M* in sodium perchlorate, which had been pre-equilibrated with water-saturated chloroform, 1.0 *M* in acetylacetone, at the desired pH. The eluant was used as the aqueous phase in a rate-determination experiment similar to those described above.

To ascertain whether the rate of transfer or the rate of formation of the extracting species was the slower process, several experiments were run. Radioactive chromium(III) perchlorate solution (50 μ l) was added to 10 ml of chloroform-saturated water, 0.1 *M* in sodium perchlorate, which had been pre-equilibrated with and then separated from 10 ml of water-saturated chloroform, 1.0 *M* in acetylacetone. The equilibration was carried out at a given pH value which was maintained throughout the succeeding reaction. The pre-equilibration was designed to give the equilibrium concentration of the acetylacetonate ion in the aqueous phase at the preset pH value. After the system had been allowed to stand for 24 h, 10 ml of water-saturated chloroform, 1.0 *M* in acetylacetone, was added and the system was agitated for 15 min. Both phases were sampled and the results were compared with regular extractions performed under analogous conditions.

RESULTS

Extractions were performed using various concentrations of acetylacetone in the organic phase, various concentrations of the metal ion, and various values of the pH. Plots of the logarithm of the ratios of the total chromium activity to the activity of chromium in the aqueous phase against time resulted in curves which showed an induction time followed by a linear portion with a slope greater than zero. The slopes were determined by the method of least squares. The first four columns of Table I present a summary of the kinetic data. Induction times varied from 90 min at a pH value of 4.0, to 5 min at a pH value of 7.0.

The fifth column of the Table presents the concentration of the acetylacetonate ion (*R*) in the aqueous phase. These values have been calculated from the following equation:

$$(R) = (HR)_0/P_r K_r (H) \quad (1)$$

In this relation $(HR)_0$ is the concentration of the acetylacetone in the chloroform, (H) is the hydrogen ion activity in the water, P_r is the organic: aqueous partition coefficient of the acetylacetone, and K_r is the association constant of the acetylacetone. Values of P_r and K_r have been taken from the literature¹³.

TABLE I
EXTRACTION RATE DATA FOR THE CHROMIUM(III)-ACETYLACETONE-CHLOROFORM SYSTEM

$(HR)_0(M)$	pH	$\log(Cr^{3+})$	$\log \text{ slope}$	$\log(R)$	$\log(R)^{\frac{1}{2}}$	k^a
1.0	5.0	-5.0	-2.9	-5.4	-2.7	1.6
1.0	4.9	-4.0	-2.9	-5.5	-2.8	1.6
1.0	4.9	-3.5	-2.9	-5.5	-2.8	1.6
1.0	4.9	-3.0	-2.9	-5.5	-2.8	1.7
1.0	4.1	-5.0	-3.3	-6.3	-3.2	1.6
1.0	5.9	-5.0	-2.4	-4.5	-2.3	1.5
1.0	7.0	-5.0	-2.0	-3.4	-1.7	1.1
3.0	5.2	-5.0	-2.4	-4.5	-2.3	1.5
0.3	5.8	-5.0	-2.9	-5.1	-2.6	1.5
0.1	5.8	-5.0	-3.1	-5.6	-2.8	1.2
0.1	7.0	-5.0	-2.7	-4.4	-2.2	0.8
0.1	7.9	-5.0	-2.8	-3.5	-1.8	0.2
1.0 ^b	4.9	-5.0	-3.5	-5.5		2000 ^c
1.0 ^b	6.0	-5.0	-2.4	-4.4		2400 ^c
1.0 ^d	5.0	-5.0	-2.3			

^a $2.3 \cdot \text{slope} \cdot (R)^{\frac{1}{2}}$.

^b Chromium(III) chloro-complex in 0.1 M NaCl.

^c $2.3 \cdot \text{slope} \cdot (R)$.

^d Chromium(III) solution passed through Jones reductor prior to extraction.

It is seen from the data of Table I that the slope (after the induction time) does not vary with increasing metal ion concentration at constant pH and constant $(HR)_0$. From this observation one can assume that the reaction is first order with respect to the chromium(III) concentration. A one-half order of the reaction with respect to $(HR)_0/(H)$ was calculated from the Van 't Hoff relation

$$n = \frac{\log [d(Cr)/dt]_1 - \log [d(Cr)/dt]_2}{\log [(HR)_0/(H)]_1 - \log [(HR)_0/(H)]_2} \quad (2)$$

where n is the order of the reaction with respect to $(HR)_0/(H)$. Corresponding ratios of $\Delta(Cr)/\Delta t$ were taken as a measure of the derivative $d(Cr)/dt$ in this equation. A similar relationship was used to demonstrate that the order of the reaction with respect to (R) at constant pH is one-half. Since $(HR)_0/(H)$ is directly proportional to (R) , these results suggest that the order of the reaction is one-half with respect to (R) and zero with respect to (H) . The last column in Table I shows values of $2.3 \text{ slope} (R)^{1/2}$ which is equivalent to the observed rate constant k . The values are constant between pH values of 4.0 and 6.0, but above 6.0 a decrease is apparent.

Chromium(III) back-extractions from a chloroform phase, 1.0 M in acetylacetonate, into aqueous phases containing 1.0 M perchloric acid, 0.1 M sodium perchlorate at a pH of 6.0, 0.1 M ethylenediaminetetraacetate at a pH of 6.0, and 0.1 M sodium hydroxide showed no extraction in any case for times up to 96 h.

The two rate determinations made with the chloro-complexes of chromium(III) from an aqueous phase, 0.1 M in sodium chloride, into chloroform containing 1.0 M acetylacetonate at pH values of 4.9 and 6.0 can be compared with those of the aquo-

complexes at the same hydrogen ion activities. Plots of $\log (Cr)_{total}/(Cr)_{aqueous}$ against time gave similar curves to those obtained for the aquo-complexes. Assuming a first order reaction with respect to the metal concentration in the aqueous phase, these reactions appear to be first order with respect to $(HR)_0/(H)$, thus differing from the aquo-complexes.

Passage of the chromium(III) solution through a Jones reductor prior to extraction resulted in a marked increase in reaction rate. At a pH value of 5.0, the rate was increased by a factor of about 3.

In the experiments designed to ascertain if the rate of diffusion or the rate of formation of the extracting species was the slower, it was found that whether the organic and aqueous phases were in continued contact or not, the extraction values were the same.

DISCUSSION

The rate of extraction of a metal chelate from an aqueous phase into an organic phase may be considered as dependent upon the rate of formation of the extracting species and the rate of transfer of this species from the aqueous to the organic phase. The last-mentioned results indicate that the formation rate is the slower one and thus it determines the overall rate in this system.

The relative inertness of the chromium system is generally to be expected. Chromium(III) compounds of all observed types have been found to have relatively little lability^{9,10}. Both the valence bond theory (inner and outer orbital considerations) and the ligand field theory (ligand field stabilization considerations) predict this behavior¹⁴.

The induction periods, which seem to be dependent upon (R) , agree with the observation of MCKAVENEY AND FREISER¹¹ that no extraction is observed in the pH range from 0.0 to 6.0 after times up to 30 min. The same investigators found no back-extraction in chromium(III)-acetylacetonate systems even into aqueous phases at very high acidities; this also agrees with the present work.

The interesting rate dependence on the square root of (R) suggests several possibilities, one of which is the presence of a polynuclear chromium(III) complex in the aqueous phase. The tendency of chromium(III) to form *ol* and *oxo* bridges is well known^{8,15}. Such a polynuclear complex might be attacked by the chelating reagent anion resulting in the displacement of water groups with the subsequent extraction of the resulting complex (perhaps still containing *ol* and/or *oxo* bridges) into the organic phase. Further investigations on the system will be necessary to resolve the apparently complicated reaction mechanism and to identify the participating species. It is possible that the extractions using the chloro-complexes did not involve polynuclear species in the rate-determining steps, this possibly explaining the rate dependence on (R) . The failure of back-extraction is not surprising since a number of neutral chelate compounds are known to exhibit a refractory character toward attack by other ligands¹⁶. This character is particularly pronounced with chromium(III).

As can be seen from the last line in the Table, prior reduction of the aqueous phase results in marked enhancement of the extraction rate. This can possibly be assigned to the greater lability of aquated chromium(II) coupled with the easy oxidation back to chromium(III).

SUMMARY

The extraction of chromium(III) from perchlorate and chloride media into chloroform containing acetylacetone has been investigated from the kinetic viewpoint. The effects of pH, reagent concentrations, and several other variables are reported.

RÉSUMÉ

Les auteurs ont examiné, du point de vue cinétique l'extraction du chrome(III), en milieu perchlorique, dans du chloroforme renfermant de l'acétylacétone. L'influence de divers facteurs (pH, concentration des réactifs, etc.) est mentionnée.

ZUSAMMENFASSUNG

Die Extraktion von Chrom-(III) aus perchlorsaurem- und salzsaurem Milieu mit Chloroform in Gegenwart von Acetylaceton wurde nach kinetischen Gesichtspunkten untersucht. Der Einfluss von pH Reagenzkonzentration und verschiedenen anderen Faktoren wird angegeben.

REFERENCES

- ¹ A. WALKLEY, *Proc. Australian Chem. Inst.*, 9 (1942) 29.
- ² H. IRVING, G. ANDREW AND E. J. RISDON, *J. Chem. Soc.*, (1949) 541.
- ³ R. W. GEIGER, *Ph. D. Thesis*, University of Minnesota, 1951.
- ⁴ C. B. HONAKER AND H. FREISER, *J. Phys. Chem.*, 66 (1962) 127.
- ⁵ G. K. SCHWEITZER AND J. R. RIMSTIJD, JR., *Anal. Chim. Acta*, 27 (1962) 389.
- ⁶ B. RUBIN AND T. HICKS, *U. S. At. Energy Comm. Report UCRL-126*, 1957.
- ⁷ R. W. TAFT, JR. AND E. H. COOK, *J. Am. Chem. Soc.*, 81 (1959) 46.
- ⁸ R. P. TAYLOR, *Ph. D. Thesis*, Princeton University, 1954; J. L. HAGUE, E. D. BROWN AND H. A. BRIGHT, *J. Res. Natl. Bur. Std.*, 47 (1951) 380.
- ⁹ H. TAUBE, *Chem. Rev.*, 50 (1952) 69.
- ¹⁰ F. BASOLO AND R. G. PEARSON, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1958.
- ¹¹ J. P. MCKAVENEY AND H. FREISER, *Anal. Chem.*, 29 (1957) 288; 30 (1958) 1965.
- ¹² G. H. MORRISON AND H. FREISER, *Solvent Extraction in Analytical Chemistry*, Wiley, New York, 1957, p. 201.
- ¹³ J. RYDBERG, *Svensk Kem. Tidskr.*, 65 (1953) 37.
- ¹⁴ F. A. COTTON AND G. WILKINSON, *Advanced Inorganic Chemistry*, Interscience, Wiley, New York, 1962, p. 548-558, 687-689.
- ¹⁵ C. L. ROLLINSON, in J. C. BAILAR, *The Chemistry of the Coordination Compounds*, Reinhold, New York, 1956, p. 448-463.
- ¹⁶ F. FEIGL, *Chemistry of Specific, Selective, and Sensitive Reactions*, Academic Press, New York, 1949, p. 623-624; *Anal. Chim. Acta*, 3 (1949) 300.

Anal. Chim. Acta, 29 (1963) 46-51

THE DETERMINATION OF TITANIUM IN METEORITIC MATERIAL

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(Received January 16th, 1963)

Titanium determinations are routinely included in complete meteorite analyses. The precision and accuracy of this determination has been far from satisfactory¹, however, probably because of the low sensitivity of the hydrogen peroxide reaction which is generally used. The much higher sensitivity exhibited by tiron² for titanium would be expected to yield an improved accuracy if the interference of iron could be overcome.

Reduction of the iron to iron(II) with ascorbic acid³ or hydroxylamine hydrochloride³ before the addition of tiron, or with sodium dithionite² after its addition, permits the determination of titanium with tiron in the presence of minor amounts of iron, and such reduction has been utilized in a simple method for the analysis of titanium in silicate rocks². These methods are inadequate, however, for the analysis of ultrabasic rocks and meteorites where 10 %/mg of iron may be present.

A method is quoted by SANDELL⁴ in which EDTA is used to complex iron and thus prevent its reaction with tiron. Although this procedure was soon shown to be unsatisfactory for the present purpose, the use of EDTA appeared promising and was therefore examined further.

Preliminary work

In the method involving disodium ethylenediaminetetraacetate (EDTA)⁴, 5 ml of a 0.05 M EDTA solution is added after the addition of tiron, so that a ferric-EDTA complex is formed. The same quantity of EDTA is added to a similar aliquot without the addition of tiron, the quantity of buffer being the same in each aliquot.

TABLE I
USE OF THE FERRIC-EDTA COMPLEX
(Absorbance at 430 m μ , 1-cm cell)

<i>TiO₂</i> (mg/50 ml)	<i>Fe absent</i>	<i>10 mg Fe present</i>	<i>Absorbance due to ferric-EDTA</i>	<i>Absorbance after correction due to ferric-EDTA</i>
0.02	0.050	0.124	0.062	0.062
0.04	0.093	0.175	0.063	0.113
0.06	0.139	0.215	—	0.153
0.10	0.220	0.308	0.060	0.246

The absorbance of the latter solution is subtracted from the former. High results were obtained when this procedure was applied to small quantities (0.02–0.10 mg) of titanium dioxide in the presence of 10 mg of iron (Table I); moreover, it was considered undesirable to have a correction equal to the absorbance given by the titanium tiron complex.

It was found that the coloured ferric–EDTA complex was reduced by the addition of sodium dithionite (50 mg) to a colourless ferrous complex which contributed no absorbance even when 10 mg of iron was present. Further work showed that the addition of the sodium dithionite before the addition of the buffer caused large reductions in the absorbance of the titanium–tiron complex. The reduction of the ferric–EDTA complex by sodium dithionite was therefore made after the addition of the buffer.

The pH of the aliquot when the tiron is added should be less than 5, to avoid possible precipitation of meta-titanic acid. The highest absorbance of the titanium–tiron complex, however, occurs above pH 5 and a buffer is therefore required to obtain the requisite pH.

It was observed that after EDTA had been added to a solution containing titanium and tiron, the addition of an acetate buffer caused colour changes in the solution. As the pH of the solution increased from 3.5 to 5.6 the colour changed from yellowish pink through pink back to yellow, although the titanium–EDTA complex is colourless and the titanium–tiron complex is yellow. Possibly, a triple complex containing titanium, tiron and EDTA was formed initially, and with increasing pH, decomposed into the required titanium–tiron complex. SHAPIRO AND BRANNOCK⁵ recommend an ammonium acetate–acetic acid buffer to give a final pH of 5.0 while SANDELL recommends a sodium acetate buffer (1 *M*) to give a final pH of 5.6.

Preliminary work had suggested that results with the ammonium acetate–acetic acid buffer were low when EDTA was present. Both buffers were then used on standard titanium solutions containing varying quantities of EDTA; the results (Table II) suggest that a triple complex, *i.e.* titanium–tiron–EDTA, was in fact formed initially and only decomposed slowly at pH 5.0 but within 5 min at pH 5.6. It is therefore preferable, when EDTA is added, to use a buffer capable of attaining a final pH of 5.6. The application to solutions containing 10 mg of iron and varying quantities of titanium dioxide is shown in Table III.

It was then possible to formulate a procedure for the determination of titanium in iron-rich materials.

TABLE II
COMPARISON OF BUFFERS
(0.11 mg TiO₂ present; absorbance at 430 m μ)

Buffer	ml of 0.05 <i>M</i> EDTA added					Time (min)
	0	1	2	3	5	
1 <i>M</i> Sodium acetate (pH 5.6)	0.249	0.249	0.249	0.249	0.249	5
Ammonium acetate–acetic acid (pH 5.0)	0.250	—	0.235	—	0.170	5
	0.250	—	0.245	—	0.208	10
	0.249	—	0.250	—	0.245	30

TABLE III
DETERMINATION OF TITANIUM IN PRESENCE OF IRON
(Absorbance at 430 m μ)

TiO_2 (mg/50 ml)	<i>Fe absent</i>	10 mg <i>Fe present as ferrous-EDTA</i>
0.02	0.050	0.050
0.04	0.093	0.095
0.06	0.139	0.140
0.10	0.220	0.220

EXPERIMENTAL

Reagents

Tiron solution. 2% Aqueous solution of catechol-3,5-disulphonic acid (1,2-dihydroxybenzene-3,5-disulphonic acid).

Standard titanium solution. 1 ml = 0.01 mg titanium dioxide. Fuse 0.01 g of Specpure titanium dioxide with AnalaR reagent potassium bisulphate (2 g) in a 50-ml platinum crucible, cool and dissolve the cake in 3% sulphuric acid, heating until a clear solution is obtained. Adjust the volume to 1 l.

Procedure

Place an aliquot containing 0.02–0.10 mg of TiO_2 in a 50-ml volumetric flask. Add 5 ml of tiron solution followed by 5 ml of 0.05 M EDTA solution. Add 10 ml of 1 M sodium acetate buffer solution, adjust the volume to 50 ml, and mix well. Just before measurement add *ca.* 50 mg of sodium dithionite and shake the flask. Measure the absorbance within 15 min at a wavelength of 430 m μ in a 1-cm cell against water. Compare the absorbance obtained with a calibration curve constructed from aliquots of the standard titanium solution treated in a similar manner. The absorbance should be measured within 15 min because decomposition of the sodium dithionite may lead to a turbidity on standing.

RESULTS AND DISCUSSION

A direct check on actual meteorites by comparing the results by the proposed method with previous determinations is not possible because of the very difficult sampling problems associated with meteoritic analysis and the frequently unreliable nature of previous titanium analyses¹. To avoid these problems, solutions of seven meteorites were prepared, and titanium was determined in aliquots by the method suggested here, and by the conventional hydrogen peroxide method. (Restriction of volumes and the use of spectrophotometer cells with 4-cm light paths were necessary to achieve adequate sensitivity with the latter method.) The results obtained are presented in Table IV. The proposed EDTA–tiron method gives values in satisfactory agreement with the results of the hydrogen peroxide method. Since it is unlikely that both methods would be subject to the same degree of interference by other constituents of the sample, it may be concluded that the method suggested is satisfactory for the direct determination of titanium in meteorites.

Although the determination of titanium in the presence of small quantities of iron

using tiron is a relatively simple procedure, the addition of EDTA to mask larger quantities of iron requires the procedure recommended above to ensure accurate results. This method allows a simple and reliable determination of titanium in meteoritic materials without prior separations.

TABLE IV
COMPARISON OF METHODS

Meteorite	Hydrogen peroxide (% TiO ₂)	Method presented (% TiO ₂)
Holbrook	0.072	0.078
Bjurbole	0.083	0.084
Zhovtevyi	0.077	0.077
Olivenza	0.073	0.071
Allegan	0.071	0.075
Elanovka	0.072	0.072
Rawlinna		0.071, 0.070, 0.072, 0.071, 0.079, 0.074 (mean 0.073)

SUMMARY

A method utilizing tiron for the determination of titanium in meteorites is described. Iron interference is avoided by formation of the ferric-EDTA complex at low pH, followed by reduction to the ferrous-EDTA complex at pH 5.6. Results for actual meteorite solutions agreed well with those obtained by the hydrogen peroxide method, thus the advantages of the greater sensitivity of tiron may be gained without loss of accuracy.

RÉSUMÉ

Une méthode est décrite pour le dosage du titane dans les météorites, au moyen de tiron. Le fer gêne; il peut être masqué par l'EDTA. Les résultats obtenus correspondent bien avec ceux obtenus par la méthode au peroxyde d'hydrogène; la sensibilité est meilleure avec le tiron.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Titan in Meteoriten unter Anwendung von Tiron. Eisen stört, kann aber mit EDTA maskiert werden. Die erhaltenen Werte stimmen gut überein mit denjenigen der Wasserstoffperoxyd-Methode, wobei jedoch das Tiron eine grössere Empfindlichkeit aufweist.

REFERENCES

- ¹ H. C. UREY AND H. CRAIG, *Geochim. Cosmochim. Acta*, 4 (1953) 36.
- ² J. H. YOE AND A. R. ARMSTRONG, *Anal. Chem.*, 19 (1947) 100.
- ³ P. N. R. NICHOLS, *Analyst*, 85 (1960) 452.
- ⁴ E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 3rd ed., 1959, 875.
- ⁵ L. SHAPIRO AND W. W. BRANNOCK, *U.S. Geol. Surv. Bull.* 1036-C, 1956, 36.

STUDIES ON THE SOLVENT EXTRACTION OF YTTRIUM THENOYLTRIFLUOROACETONATE

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(Received January 9th, 1963)

Very little detailed work has been carried out on the solvent extraction behavior of yttrium chelates. Observations of yttrium extractions using such diverse reagents as oxine¹, tropolone², isopropyltropolone³, acetylacetone⁴, and benzoylacetone⁵ have been reported. The extraction of yttrium, as well as 52 other metals, into organic solvents containing thenoyltrifluoroacetone has been described in a review by POSKANZER AND FOREMAN⁶. This summary purportedly covers the literature to 1960.

Extraction equations

If one considers the extraction of the hydrated yttrium(III) ion from an aqueous solution into an organic solvent containing thenoyltrifluoroacetone represented as HR, the following equation may be written:

$$D = K_o P_o (HR)_o^3 / K_r^3 P_r^3 (H)^3 Q = K (HR)_o^3 / (H)^3 Q \quad (1)$$

In this relationship, the predominant extracting species is assumed to be YR₃, *D* is the organic:aqueous distribution ratio of the total metal concentration in the organic phase to that in the aqueous phase, *P_o* is the organic:aqueous distribution coefficient of YR₃, *P_r* is the organic:aqueous distribution coefficient of HR, *K_o* is the association constant of YR₃, *K_r* is the association constant of HR, (HR)_o is the equilibrium concentration of HR in the organic phase, (H) is the hydrogen ion concentration in the aqueous phase, *Q* is a term which is intended to account for the presence of species other than the simple hydrated yttrium(III) ion in the aqueous phase, and *K* is the extraction constant which is equal to *K_oP_o/K_r³P_r³*. The term *Q*, known as the aqueous complexing term, might take the following form:

$$Q = 1 + K_1(OH) + K_2(OH)^2 + K_3(OH)^3 + K_4(OH)^4 + K_5(OH)^5 \\ + K_6(OH)^6 + K_a(R) + K_b(R)^2 + K_c(R)^3 \quad (2)$$

In this exemplary equation, *K₁*, *K₂*, *K₃*, *K₄*, *K₅* and *K₆* are the successive cumulative association constants for simple complexes between the yttrium(III) ion and the hydroxide ion, (OH) is the equilibrium concentration of the hydroxide ion, *K_a*, *K_b* and *K_c* are the successive cumulative association constants for complexes between the yttrium(III) ion and the thenoyltrifluoroacetone ion, and (R) is the equilibrium

concentration of this latter ion. In this form of Q , all mixed complexes are ignored, and no species other than YR_3 is considered as extracting into the organic phase.

Taking logarithms of equation (1), the following is obtained:

$$\log D = \log K + 3 \log (HR)_0 - 3 \log (H) - \log Q \quad (3)$$

For systems in which the simple hydrated yttrium(III) ion is the predominant aqueous species, Q will be equal to 1. Therefore plots of $\log D$ against pH at constant $(HR)_0$ and of $\log D$ against $\log (HR)_0$ at constant pH will both give slopes of 3. For systems containing appreciable $Y(OH)^{2+}$ in addition to Y^{3+} in the aqueous phase, Q , will become $1 + K_1(OH)$. When the amount of $Y(OH)^{2+}$ becomes much larger than Y^{3+} , $K_1(OH)$ is considerably greater than 1, and Q will be approximately equal to $K_1(OH)$. In this latter case, equation (3) can be modified to read as follows:

$$\begin{aligned} \log D &= \log K + 3 \log (HR)_0 - 3 \log (H) - \log K_1(OH) \\ &= \log K + 3 \log (HR)_0 - 2 \log (H) - \log K_1 K_w \end{aligned} \quad (4)$$

In this relation K_w is the ion product of water. Thus a plot of $\log D$ against pH at constant $(HR)_0$ should show a slope of 2, and a plot of $\log D$ against $\log (HR)_0$ at constant pH should show a slope of 3.

Present problem

In this work, the extraction of yttrium ion from aqueous solutions into organic solvents containing thenoyltrifluoroacetone at several different concentrations was studied in order to determine the predominant aqueous-phase species of the metal under various conditions. Several organic solvents and mixtures of the solvents were employed, and P_e values for YR_3 were determined for each solvent system. Data from these extractions allowed estimates to be made of stability constants for YR_3 and $Y(OH)^{2+}$.

EXPERIMENTAL

The chemicals, apparatus, and general procedures were essentially the same as described in previous work^{7,8}. Ten-ml portions of the aqueous phase were stirred with 10 ml of the organic phase for 9 h at $30.0 \pm 0.5^\circ$. In all extractions the original yttrium concentration in the aqueous phase was approximately $10^{-6} M$ and was radioactively labelled with yttrium-91 to facilitate measurement of the extraction. All experiments were carried out in a perchlorate medium with an ionic strength of 0.1. Values of pH were measured with a Beckman Model H2 pH Meter in conjunction with a Beckman Combination Electrode.

Values of P_e were found by equilibrating a 5-ml portion of the organic phase containing yttrium thenoyltrifluoroacetone with a 15-ml portion of $10^{-1} M$ sodium perchlorate solution at a proper pH value. After equilibration, aliquots of each phase were evaporated to dryness and counted, and the P_e value was calculated. Each value represents the average of at least three determinations.

RESULTS AND DISCUSSION

Table I summarizes the extraction results of this study. All reported curves were plotted as per cent extraction against pH, at least 10 points being determined for each curve. All curves showed the familiar sigmoid shape. The $pH_{1/2}$ values represent

TABLE I
SUMMARY OF DATA FOR VARIOUS EXTRACTION SYSTEMS

System ^a	$pH_{1/2}$	$\log P_e$	$\log P_r$
Chloroform containing 0.3 M HR: pH (% E), 3.0 (11), 3.0 (12), 3.1 (15), 3.1 (18), 3.4 (65), 3.5 (78), 3.5 (79), 3.8 (95), 3.9 (99), 4.3 (99)	3.3	—	1.8
Chloroform containing 0.1 M HR: 2.8 (1), 2.9 (2), 3.4 (10), 3.6 (37), 3.8 (55), 3.9 (60), 4.0 (76), 4.1 (87), 4.1 (88), 4.3 (95), 4.6 (97)	3.8	3.4	1.8
Chloroform containing 0.03 M HR: 3.1 (1), 3.5 (1), 3.6 (3), 3.7 (5), 3.9 (9), 3.9 (14), 4.0 (19), 4.4 (56), 4.5 (63), 4.6 (71), 4.9 (89), 4.9 (92), 5.0 (94), 5.3 (96), 5.5 (97)	4.4	—	1.8
Chloroform containing 0.01 M HR: 3.5 (1), 3.7 (1), 3.9 (3), 4.4 (14), 4.4 (16), 4.5 (21), 4.7 (24), 4.8 (40), 4.8 (55), 4.8 (58), 5.0 (73), 5.0 (77), 5.2 (84), 5.2 (86), 5.3 (92), 5.5 (95), 5.8 (96), 6.0 (98)	4.8	—	1.8
Chloroform containing 0.003 M HR: 4.7 (1), 5.1 (11), 5.3 (28), 5.6 (60), 5.8 (80), 5.8 (81), 6.0 (90), 6.1 (93), 6.2 (94), 6.4 (96), 6.5 (99)	5.5	—	1.8
Chloroform containing 0.001 M HR: 5.2 (6), 5.2 (8), 5.3 (12), 5.4 (20), 5.8 (59), 5.8 (60), 6.1 (88), 6.3 (91), 6.3 (93), 6.4 (96), 6.5 (96)	5.8	—	1.8
Benzene containing 0.3 M HR: 2.4 (4), 2.6 (16), 2.6 (25), 2.8 (35), 2.9 (43), 3.2 (84), 3.3 (91), 3.6 (98), 3.9 (97)	2.9	—	1.6
Benzene containing 0.1 M HR: 2.8 (3), 3.1 (17), 3.2 (34), 3.2 (34), 3.3 (47), 3.6 (83), 3.7 (87), 3.8 (83), 3.9 (96), 4.3 (97), 4.5 (99)	3.3	3.9	1.6
Benzene containing 0.03 M HR: 3.1 (2), 3.4 (8), 3.6 (23), 3.7 (40), 4.0 (67), 4.0 (72), 4.2 (86), 4.4 (91), 4.9 (97), 5.4 (99), 5.5 (99)	3.8	—	1.6
Benzene containing 0.01 M HR: 3.7 (5), 3.9 (7), 4.1 (14), 4.2 (18), 4.3 (27), 4.4 (50), 4.6 (74), 4.6 (81), 4.8 (87), 5.3 (98), 5.4 (99)	4.4	—	1.6
Benzene containing 0.003 M HR: 4.2 (1), 4.4 (6), 4.7 (18), 4.8 (27), 4.9 (34), 5.1 (68), 5.2 (66), 5.3 (72), 5.4 (81), 5.5 (84), 5.7 (93), 5.8 (93), 6.2 (97)	5.0	—	1.6
Benzene containing 0.001 M HR: 4.7 (5), 5.1 (20), 5.2 (30), 5.3 (44), 5.3 (60), 5.5 (74), 5.6 (79), 5.7 (86), 5.8 (87), 5.9 (94), 6.0 (97)	5.3	—	1.6
MIBK containing 0.3 M HR: 1.5 (1), 1.6 (2), 1.8 (5), 2.1 (28), 2.3 (45), 2.5 (79), 2.7 (91), 3.0 (99), 3.1 (99), 3.1 (100)	2.3	—	1.2
MIBK containing 0.1 M HR: 1.8 (1), 2.0 (2), 2.2 (3), 2.9 (7), 2.6 (28), 2.7 (39), 2.8 (52), 2.9 (67), 3.0 (76), 3.2 (95), 3.3 (96), 4.0 (99)	2.8	4.2	1.2
MIBK containing 0.03 M HR: 2.7 (1), 3.1 (18), 3.2 (25), 3.3 (47), 3.3 (50), 3.5 (76), 3.6 (82), 3.7 (88), 3.9 (96), 4.0 (99)	3.3	—	1.2
MIBK containing 0.01 M HR: 3.0 (1), 3.3 (5), 3.5 (11), 3.6 (15), 3.7 (35), 3.7 (37), 3.8 (53), 3.9 (67), 4.1 (89), 4.2 (93), 4.4 (98)	3.8	—	1.2
MIBK containing 0.003 M HR: 3.5 (1), 3.8 (5), 3.9 (7), 4.1 (16), 4.2 (35), 4.3 (46), 4.3 (52), 4.3 (57), 4.4 (64), 4.5 (76), 4.5 (80), 4.6 (88), 4.7 (93), 4.9 (98)	4.3	—	1.2
MIBK containing 0.001 M HR: 3.9 (1), 4.2 (2), 4.4 (5), 4.6 (10), 4.6 (13), 4.7 (26), 4.8 (33), 4.9 (50), 4.9 (53), 5.1 (73), 5.2 (77), 5.2 (80), 5.3 (88), 5.6 (95), 5.7 (97), 6.1 (99)	4.9	—	1.2

TABLE I (continued)

System ^a	$pH_{1/2}$	$\log P_e$	$\log P_r$
50 mole % MIBK in benzene containing 0.1 M HR: 2.3 (6), 2.4 (11), 2.6 (28), 2.7 (37), 2.8 (53), 2.9 (65), 3.0 (92), 3.2 (96), 3.6 (99)	2.8	4.2	—
25 mole % MIBK in benzene containing 0.1 M HR: 2.3 (1), 2.5 (3), 2.6 (8), 2.7 (40), 2.8 (55), 2.9 (68), 3.1 (94), 3.5 (99), 4.0 (100)	2.8	4.0	—
50 mole % MIBK in chloroform containing 0.1 M HR: 2.4 (6), 2.5 (12), 2.6 (19), 2.7 (41), 2.9 (59), 2.9 (63), 3.1 (88), 3.2 (92), 3.3 (96), 3.7 (100)	2.8	4.2	—
25 mole % MIBK in chloroform containing 0.1 M HR: 2.2 (1), 2.4 (4), 2.7 (25), 2.9 (59), 3.2 (90), 3.4 (96), 3.6 (99)	2.8	4.2	—
50 mole % benzene in chloroform containing 0.1 M HR: 2.9 (4), 3.3 (33), 3.4 (49), 3.5 (56), 3.6 (78), 3.8 (93), 3.9 (95), 4.1 (98)	3.4	3.8	—
Chloroform containing 0.1 M HR, aqueous phase containing 2 volume % <i>n</i> -butylamine: 2.6 (2), 2.8 (6), 3.0 (15), 3.1 (25), 3.1 (27), 3.2 (54), 3.2 (55), 3.4 (76), 3.4 (78), 4.1 (100)	3.2	2.5	—
Chloroform containing 0.1 M HR, aqueous phase containing 10 volume % <i>n</i> -butylamine: 2.1 (1), 2.3 (1), 2.7 (10), 3.0 (50), 3.2 (80), 3.3 (94), 3.5 (97), 3.7 (99), 4.0 (100), 4.2 (100)	3.0	—	—
Chloroform containing 0.01 M HR, aqueous phase containing 2 volume % <i>n</i> -butylamine: 3.7 (2), 3.8 (2), 4.1 (14), 4.2 (33), 4.4 (67), 4.5 (75), 4.6 (91), 4.8 (97), 4.9 (98), 5.0 (100)	4.3	—	—
Chloroform containing 0.001 M HR, aqueous phase containing 2 volume % <i>n</i> -butylamine: 4.7 (1), 4.9 (4), 5.4 (45), 5.4 (52), 5.6 (67), 5.6 (74), 5.7 (82), 5.8 (95), 6.0 (95), 6.0 (98), 6.1 (99), 6.3 (100)	5.4	—	—
Chloroform containing 0.001 M HR, aqueous phase containing 0.01 M F ⁻ : 5.7 (1), 5.8 (1), 6.0 (2), 6.2 (14), 6.6 (58), 6.6 (61), 6.7 (79), 6.8 (90), 7.1 (96), 7.3 (97)	6.5	—	—

^a The figures in parentheses represent per cent extraction values. The figures preceding the parentheses represent the corresponding pH values.

the pH values at which one-half of the metal has been extracted into the organic phase (that is, $D = 1$). Below a pH of approximately 4.0, plots of $\log D$ against pH at constant $(HR)_0$ gave slopes of 3, and plots of $\log D$ against $\log (HR)_0$ at constant pH also gave slopes of 3. This is indicative of the dominance in the organic phase of YR_3 and of Y^{3+} in the aqueous phase. From the benzene data using $\log P_r$ as 1.6⁶ and $\log K_r$ as 6.4⁶ plus D , pH, and P_e as determined experimentally, a value of 13.2 for $\log K_e$ was obtained. By analogous calculations, values of 13.1 and 13.2 were obtained in the chloroform and methyl isobutyl ketone systems respectively.

For extractions occurring above a pH of about 4.0, plots of $\log D$ against pH at constant $(HR)_0$ gave slopes of 2, whereas plots of $\log D$ against $\log (HR)_0$ at constant pH gave slopes of 3. These phenomena were interpreted as indicating the dominant species in the organic phase to be YR_3 and that in the aqueous phase to be $Y(OH)^{2+}$. Calculations employing equation (4) yielded an average value for $\log K_1$ of about 9.

The results of this study indicate that methyl isobutyl ketone is the best solvent of the three studied for the extraction of yttrium thenoyltrifluoroacetate by virtue of the high P_e and low P_r values seen in this system. However, mixtures containing

50 mole per cent and even 25 mole per cent of methyl isobutyl ketone in chloroform and in benzene gave the same $pH_{1/2}$ and P_c values as did pure methyl isobutyl ketone. These data would appear to indicate a fairly weak association between the yttrium thenoyltrifluoroacetate and methyl isobutyl ketone. Such an association might involve a coordination number of at least seven for yttrium. However, since a coordination number of seven has been demonstrated for scandium in certain instances⁹, this would seem entirely possible for the larger yttrium ion. Some unpublished data of DYRSSEN AND SEKINE¹⁰ support this interpretation.

Two volume per cent of *n*-butylamine was added to chloroform for some extractions in order to determine if an adduct between the yttrium thenoyltrifluoroacetate and the amine would be formed. Apparently no such adduct was formed in the pH range used, since the measured log P_c into chloroform was only 2.5, a 10-fold decrease from the value in pure chloroform. The extraction was shifted to a lower $pH_{1/2}$, however, and it is suspected that this shift is due to a decrease in P_r , that is, more chelating reagents partitions into the aqueous phase by virtue of the presence of the *n*-butylamine. The addition of 10 volume per cent of the amine shifts the extraction to even lower pH values.

The addition of *n*-butylamine to systems in the pH range where hydrolysis is important not only shifts the extraction to lower pH values but also changes the slope of log D vs. pH curves from 2 to 3. Thus it would seem that the *n*-butylamine (B) might be successfully competing with the hydroxide ion to form an aqueous complex of the type YB_n^{3+} which is broken in the extraction step. Similar behavior with regard to the slope change was noted when a good complexing agent, fluoride ion, was added to the aqueous phase. The extraction itself, however, was shifted to higher pH values, as was expected.

SUMMARY

Studies of extractions of yttrium from aqueous solution into chloroform, benzene, methyl isobutyl ketone, and mixtures of these solvents, containing thenoyltrifluoroacetone are described. The effects of reagent concentration, added *n*-butylamine, and added fluoride were investigated. Values of $pH_{1/2}$ and P_c were determined, and identifications of the involved species are suggested.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction de l'yttrium dans le chloroforme, le benzène, la méthylisobutylcétone et de mélanges de ces solvants, renfermant de la thénoyltrifluoracétone. Ils ont examiné également l'influence de la concentration du réactif, de la butylamine et des fluorures.

ZUSAMMENFASSUNG

Es wird eine Untersuchung beschrieben über die Extraktion von Yttrium aus wässriger Lösung mit Chloroform, Benzol, Methyl-isobutylketon und Gemischen dieser Lösungsmittel in Gegenwart von Thenoyltrifluoroacetone. Der Einfluss der Reagenzkonzentration, Zusatz von Butylamin und Fluoriden wurde ebenfalls untersucht.

REFERENCES

- 1 N. P. RUDENKO, *Zh. Neorgan. Khim.*, 4 (1959) 220.
- 2 J. RYDBERG, *Svensk Kem. Tidskr.*, 67 (1955) 499.
- 3 D. DYRSSEN, *Trans. Roy. Inst. Technol. Stockholm*, 188 (1962) 28.
- 4 M. TABUSHI, *Bull. Inst. Chem. Res. Kyoto Univ.*, 37 (1959) 252.
- 5 J. STARY AND N. P. RUDENKO, *Zh. Neorgan. Khim.*, 4 (1959) 2405.
- 6 A. M. POSKANZER AND B. M. FOREMAN, JR., *J. Inorg. & Nucl. Chem.*, 16 (1961) 323.
- 7 G. K. SCHWEITZER AND F. F. DYER, *Anal. Chim. Acta*, 22 (1960) 172.
- 8 G. K. SCHWEITZER AND G. R. COE, *Anal. Chim. Acta*, 24 (1961) 311.
- 9 L. POKRAS, M. KILPATRICK AND P. M. BERNAYS, *J. Am. Chem. Soc.*, 75 (1953) 1254.
- 10 D. DYRSSEN AND T. SEKINE, private communication.

POLAROGRAPHIC DETERMINATION OF INDIUM IN LEAD AND ZINC METALS*

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(Received January 21st, 1963)

A study of the distribution of indium between molten lead and zinc required the analysis of a large number of samples containing low milligram quantities of indium in lead metal containing 2% of zinc and in zinc metal containing 2% of lead. A polarographic procedure promised to be the most rapid, as no prior separations other than the precipitation of the lead would be needed.

The method of ZOTTA¹, previously used successfully by the present authors for the determination of cadmium in similar lead and zinc equilibration studies, failed in this case because the indium break "tailed-off" badly into the region of the zinc break. According to tabulated values in the literature², indium has a half-wave potential of -1.13 V in 1 M sodium hydroxide solution. In agreement with the work of RIENÄCKER AND HOSCHER³, we could not obtain any useful polarograms in this medium.

The methods suggested by DESESA *et al.*⁴ and by KOLTHOFF AND LINGANE⁵ were not applicable in the presence of sulfate.

The use of a 0.1 M solution of ammonium thiocyanate as the supporting electrolyte for the determination of indium⁶ gave 100% recovery of indium in synthetic samples of lead metal containing 2% of zinc but gave only 91 to 98% recovery of the indium from synthetic samples of zinc metal containing 2% of lead.

RIENÄCKER AND HOSCHER³ and JENTZSCH *et al.*⁷ have used tartaric acid for the polarographic determination of indium. In both of these cases, zinc was separated from the indium prior to the recording of the polarogram. In the procedure outlined below, lead was precipitated with sulfuric acid and the indium determined without separating any of the zinc, although the zinc to indium ratio was greater than 350:1 in some cases.

EXPERIMENTAL

Apparatus

The polarograms were obtained with the Metrohm recording Polarecord E 261 supplied in this country by Brinkman Instruments Inc. The cell was an EA 668 supplied with a water jacket. Constant temperature was maintained by use of the

* Contribution No. 1277. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

Gebrüder Haake Thermostat, Type "F." Potentials were measured *vs.* a silver-silver chloride-saturated potassium chloride reference electrode as recommended by Metrohm and supported by MEITES⁸. Potential values were then calculated *vs.* the S.C.E. for convenience of comparison.

Reagents

Standard indium solutions were prepared by dissolving, in a minimum of nitric acid, 99.99% pure metal obtained from Fisher Scientific Company. For interference studies, the lead metal used was granular lead (L-24) obtained from Fisher Scientific Company while the zinc was 99.99% pure electrolytic zinc obtained from the Bunker Hill Company. The mercury was triply cleaned and distilled. Reagent-grade D-tartaric acid was used. Distilled water which was passed through a mixed-bed ion exchanger was used throughout. Knox gelatin was used in the thiocyanate procedure.

Effect of pH

The optimum pH was found to be 2.0.

Effect of time

RIENÄCKER AND HOSCHER⁹ recommended that solutions of indium be allowed to stand for 1 h between the adjustment of the pH and the deaeration period. However, no variation in the recovery of indium was observed when this waiting period was varied from 3 min to about 18 h under the conditions of our procedure.

Effect of tartaric acid concentration

Results were found to be dependent upon the tartaric acid concentration in the final solution. Precipitates formed in solutions of 12, 15, 20 and 25% upon adjustment of pH. At 5%, inconsistent results were obtained; 8% and 10% solutions were found to be satisfactory, but results showed that some one definite concentration must be used consistently. A final concentration of 10% D-tartaric acid was maintained in all solutions used for the preparation of the wave height-concentration plot and for all other results.

Tartaric acid procedure

Dissolve the sample in a minimum amount of 1:1 nitric acid. Place in an appropriate volumetric flask. Add 25 ml of sulfuric acid per 500-ml volume. Leave the precipitate of lead sulfate in the flask. Place a 5-ml aliquot (preferably 0.1 to 2.5 mg In) of this solution in a 50-ml beaker. Add 20 ml of a 12.5% solution of D-tartaric acid. Adjust the pH to 2.0 with concentrated ammonium hydroxide. Keep the temperature at $25.0 \pm 0.3^\circ$. Deaerate the solution for 10 min in the water-jacketed cell by passing helium gas through the solution. During the recording of the polarogram, pass helium gas over the solution. Use Tygon tubing to prevent any air from diffusing into the helium gas as it is transferred from the tank to the cell⁹. Record the polarogram from -0.5 to -1.0 V. For interpretation of the waves, use the average of the oscillations as recommended by MEITES¹⁰ and ZUMAN AND KOLTHOFF¹¹. Determine indium present by comparison to a wave height-concentration plot prepared in the same manner.

Thiocyanate procedure

Dissolve the sample in a minimum amount of 1:1 nitric acid. Place in an appropriate volumetric flask. Add 25 ml of concentrated sulfuric acid per 500-ml volume. Leave the precipitate of lead sulfate in the flask. Fume a suitable aliquot (preferably 0.1 to 2.0 mg In) to near dryness. Take care not to bake the sample. Pipet 25.0 ml of electrolyte (0.1 M ammonium thiocyanate with 0.005% gelatin) into the beaker to dissolve the residue. Adjust the pH to 1.0 ± 0.1 with concentrated sulfuric acid. Continue as described in the tartaric acid procedure.

RESULTS

Except where listed as otherwise, sharp breaks were obtained which were quite easy to measure.

With 64 determinations of indium alone by this method, the standard deviation was 1.79%. The indium concentration varied from 0.163 mg to 2.71 mg per 25 ml.

The wave height *vs.* concentration plot was linear. Irreversibility for the electrode process was indicated by the non-linear plots for $\log(i_a - i)/i$ *vs.* E_{ae} and the change of half-wave potential with concentration. For the 10^{-5} M concentration range, the half-wave potential (*vs.* S.C.E.) changed from -0.750 V at $5.7 \cdot 10^{-5}$ M to -0.752 V at $9.4 \cdot 10^{-5}$ M. For the 10^{-4} M concentration range, the half-wave potential (*vs.* S.C.E.) changed from -0.758 V at $1.9 \cdot 10^{-4}$ M to -0.812 V at $9.4 \cdot 10^{-4}$ M.

Table I shows that the presence of zinc has little effect on the recovery of indium.

TABLE I
DETERMINATION OF INDIUM IN THE PRESENCE OF ZINC

Zinc added (mg)	Indium added (mg)	Indium recovered	
		(mg)	(%)
4.20	0.542	0.555	102.4
4.20	0.542	0.551	101.7
4.22	2.71	2.755	101.7
4.22	2.71	2.755	101.7
36.75	0.542	0.542	100.0
36.75	0.542	0.548	101.3
37.2	2.71	2.755	101.7
37.2	2.71	2.744	101.2
77.66	0.542	0.547	100.9
77.66	0.542	0.547	100.9
77.66	0.542	0.533	98.3
78.4	2.71	2.711	100.0
78.4	2.71	2.733	100.8
140.25	0.542	0.542	100.0
140.25	0.542	0.538	99.3
140.25	0.542	0.536	98.9
144.0	2.71	2.658	98.1
144.0	2.71	2.711	100.0
144.0	2.71	2.722	100.4
		Av. % recovery =	100.5
		Standard deviation =	1.211

The results for some synthetic samples closely approximating the samples received with lead and zinc present are recorded in Table II.

TABLE II
DETERMINATION OF INDIUM IN THE PRESENCE OF ZINC AND LEAD

Zinc taken (mg)	Lead taken (mg)	Indium taken (mg)	Indium recovered	
			(mg)	(%)
72.15	1.40	0.813	0.822	101.1
70.57	1.52	1.35	1.373	101.7
70.57	1.52	1.35	1.360	100.7
70.57	1.52	1.35	1.333	98.7
70.57	1.52	1.35	1.364	101.0
3.52	140.77	0.813	0.822	101.1
3.39	141.45	0.542	0.562	103.7
3.16	141.52	1.08	1.111	102.9
3.92	141.88	1.35	1.378	102.1
3.92	141.88	1.35	1.382	102.4
			Av. % recovery =	101.5
			Standard deviation =	1.372

Table III shows that the tartaric acid procedure and the thiocyanate procedure both give satisfactory results for indium in lead metal containing 2% of zinc.

TABLE III
DETERMINATION OF INDIUM IN LEAD WITH 2% OF ZINC

Thiocyanate procedure ^a		Tartaric acid procedure ^b	
Indium (mg)	Indium (%)	Indium (mg)	Indium (%)
52	0.38	50.9	0.368
164	1.165	165.3	1.173
165	1.265	164.4	1.262
180	1.295	178.2	1.284
187	1.24	184.4	1.225
190	1.255	187.6	1.237
178	1.27	176.9	1.265
179	1.23	176.4	1.213
159	1.11	158.7	1.108
165	1.19	162.2	1.171
171	1.215	170.2	1.211

^a Determined by Analyst A.

^b Determined by Analyst B.

The tartaric acid procedure affords a rapid means for the polarographic determination of indium in lead metal containing 2% of zinc and in zinc metal containing 2% of lead with sufficient accuracy and precision for routine work.

The authors wish to thank C. P. LIND for performing the analyses by the thiocyanate procedure.

SUMMARY

A rapid polarographic method for determining low milligram quantities of indium in lead metal containing 2% of zinc and in zinc metal containing 2% of lead is described. In a supporting electrolyte of 10% D-tartaric acid adjusted to pH 2.0, a well-defined wave for indium is obtained after the precipitation of lead as the sulfate.

RÉSUMÉ

Une méthode est décrite pour le dosage polarographique rapide de l'indium dans le plomb, renfermant 2% de zinc et dans le zinc, renfermant 2% de plomb. En utilisant une solution d'acide *d*-tartrique à 10%, ajustée au pH 2, on obtient une vague bien définie pour l'indium, après précipitation du plomb comme sulfate.

ZUSAMMENFASSUNG

Beschreibung einer raschen polarographischen Methode zur Bestimmung von Indium in Blei mit 2% Zink und in Zink mit 2% Blei. In einer 10%igen Lösung von D-Weinsäure und einem pH = 2 erhält man nach Fällung des Bleies als Sulfat eine gut definierte Stufe für das Indium.

REFERENCES

- ¹ M. ZOTTA, *Gazz. Chim. Ital.*, 78 (1948) 143.
- ² J. HEYROVSKY AND D. ILKOVIC, *Collection. Czech. Chem. Commun.*, 7 (1935) 198.
- ³ V. G. RIENÄCKER AND E. HOSCHEK, *Z. Anorg. Allgem. Chem.*, 268 (1952) 260.
- ⁴ M. A. DESESA, D. N. HUME, A. C. GLAMM AND D. D. DEFORD, *Anal. Chem.*, 25 (1953) 983.
- ⁵ I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Interscience, New York, 1952, p. 519.
- ⁶ S. L. PHILLIPS AND E. MORGAN, *Anal. Chem.*, 33 (1961) 1192.
- ⁷ D. JENTZSCH, I. FROTSCHER, G. SCHWERDTFEGER AND G. SARFERT, *Z. Anal. Chem.*, 144 (1955) 8.
- ⁸ L. MEITES, *Polarographic Techniques*, Interscience, New York, 1955, p. 27.
- ⁹ L. MEITES, *Polarographic Techniques*, Interscience, New York, 1955, p. 34.
- ¹⁰ L. MEITES, *Polarographic Techniques*, Interscience, New York, 1955, p. 63.
- ¹¹ P. ZUMAN AND I. M. KOLTHOFF, *Progress in Polarography*, Interscience, New York, 1962, p. 586.

Short Communications

Etude thermogravimétrique des picolates et dipicolates de lanthane, praséodyme et néodyme

Au cours d'un travail d'ensemble effectué sur les picolates et dipicolates de terres rares, nous avons étudié les produits cristallisés et suivi leur décomposition thermique par analyse thermogravimétrique.

MODE OPÉRATOIRE

Préparation des produits

L'acide picolique (pyridine 2-carboxylique) est préparé par oxydation permanganique de l' α -picoline suivant la méthode de BLACK, DEPP ET CORSON¹.

L'acide 2,6-dipicolique est un produit commercial recristallisé dans l'eau.

Les oxydes de terres rares purs "Pechiney-St.-Gobain" sont dissous dans un excès d'acide perchlorique pour obtenir les solutions de perchlorates utilisées dans la précipitation.

Les picolates sont précipités par addition de soude à un mélange acide de solutions d'acide picolique et de perchlorate de terre rare dont les concentrations sont dans le rapport molaire 3/1. Le pH final de précipitation est maintenu à 4,6, valeur déduite des courbes de titration potentiométrique.

La précipitation des dipicolates conduit à deux composés différents selon le pH; l'une est effectuée à pH 3: on ajoute, dans le rapport molaire 2/1, une solution de dipicolate de sodium à une solution acide (pH < 1) de perchlorate de terre rare et ajuste le pH par addition de soude. La cristallisation est facilitée par chauffage à 80°.

Dans les mêmes rapports de concentration, à partir d'une solution de perchlorate de terre rare, de pH 2. 5-3, on précipite à pH 6 un dipicolate de composition différente du précédent. Les précipités sont ensuite filtrés, lavés et séchés 24 h par aspiration d'air.

Analyse thermogravimétrique

L'étude a été effectuée dans l'air à l'aide de la thermobalance Chevenard à enregistrement photographique. Le poids initial était d'environ 300 mg et la vitesse de chauffage 150°/h.

Des courbes obtenues, on déduit la composition des produits anhydres et éventuellement celle des composés intermédiaires par mesure des pertes de poids correspondantes et comparaison des pourcentages expérimentaux et théoriques d'oxyde: La₂O₃, Pr₆O₁₁, Nd₂O₃. La nature et la pureté des oxydes obtenus ainsi en fin de calcination ont été testées par des clichés D.S. de diffraction X comparés aux fiches A.S.T.M.

Le nombre de molécules d'eau d'hydratation s'obtient également par mesure sur la courbe de la hauteur du premier palier; on rapporte ensuite le poids calculé correspondant au poids de produit anhydre.

RÉSULTATS

Les courbes obtenues ont sensiblement la même allure pour les composés des trois cations étudiés. Elles sont reproduites dans les Fig. : 1, 2 et 3.

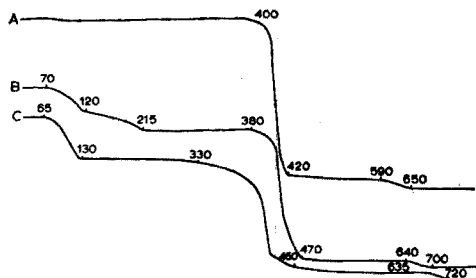


Fig. 1. A, Picolate de lanthane; B, Dipicolate de lanthane précipité à pH 6; C, Dipicolate de lanthane précipité à pH 3.

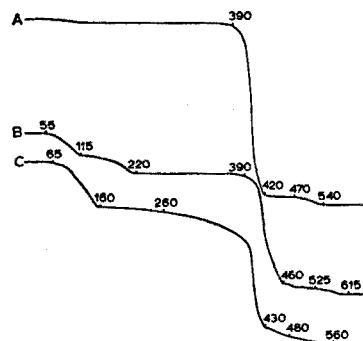


Fig. 2. A, Picolate de praséodyme; B, Dipicolate de praséodyme précipité à pH 6; C, Dipicolate de praséodyme précipité à pH 3.

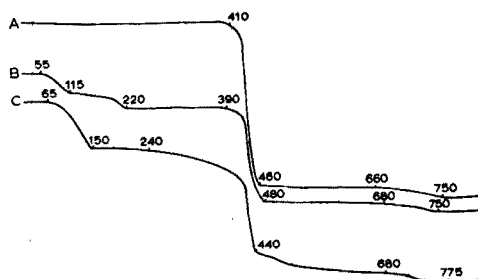


Fig. 3. A, Picolate de néodyme; B, Dipicolate de néodyme précipité à pH 6; C, Dipicolate de néodyme précipité à pH 3.

On observe successivement la déshydratation en une ou deux étapes du produit initial qui conduit au palier du produit anhydre, puis la décomposition brutale de ce dernier en un composé intermédiaire que nous avons identifié avec le dioxymonocarbonate de formule $\text{Ln}_2\text{O}_3, \text{CO}_2$ ($\text{Ln} = \text{La}, \text{Pr}$ ou Nd), et enfin l'obtention d'oxyde.

L'ensemble des résultats est résumé dans le Tableau I qui donne la formule et la couleur des produits étudiés, ainsi que les températures caractéristiques:

t_1 : température de début de déshydratation.

t_2 : température de début de décomposition des produits anhydres.

t_3 : température de début de décomposition des dioxymonocarbonates.

t_4 : température d'obtention des oxydes.

CONCLUSIONS

Les trois picolates de lanthane, néodyme et praséodyme précipitent anhydres et leur composition correspond à la formule $\text{Ln}(\text{C}_6\text{H}_4\text{O}_2\text{N})_3$.

Les dipicolates obtenus à pH 6 ont pour formule $\text{Ln}_2(\text{C}_7\text{H}_5\text{O}_4)_3 \cdot 8 \text{H}_2\text{O}$, les 8

TABLEAU I
RÉSULTATS DE L'ANALYSE THERMOGRAVIMÉTRIQUE

Formule	Couleur	t_1 (°)	% H ₂ O		t_2 (°)	t_3 (°)	t_4 (°)	% Oxyde Prod. anhyd.		Couleur carbo- nate	% Oxyde carbonate	
			Mes.	Théor.				Mes.	Théor.		Mes.	Théor.
La(pic) ₃	blanc				410	660	750	32.59	32.28	blanc	87.5	88.1
La(dipic) ₂ H, 5 H ₂ O	blanc	65	16.8	15.9	240	680	775	35.03	34.68	blanc	89.8	88.1
La ₂ (dipic) ₃ , 8 H ₂ O	blanc	55 115	15.65	15.10	390	680	750	42.21	42.17	blanc	88.1	88.1
Pr(pic) ₃	vert				390	470	540	33.3	33.6	jaune clair	90.13	91.09
Pr(dipic) ₂ H, 5 H ₂ O	vert	65	16.97	16.01	260	480	560	35.66	36.09	jaune clair	91.06	91.09
Pr ₂ (dipic) ₃ , 8 H ₂ O	vert	55 115	15.36	15.64	390	525	615	43.78	43.84	jaune clair	92.66	91.09
Nd(pic) ₃	rose pâle				400	590	650	32.5	32.9	bleu clair	88.2	88.42
Nd(dipic) ₂ H, 5 H ₂ O	rose pâle	65	17.68	16.07	330	635	720	35.12	35.4	bleu clair	90.0	88.42
Nd ₂ (dipic) ₃ , 8 H ₂ O	rose pâle	70 120	15.6	15.53	380	640	700	42.8	42.91	bleu clair	87.78	88.42

* H pic désigne l'acide picolique: C₆H₄N-COOH; H₂ dipic, l'acide dipicolique: C₆H₃N(COOH)₂.

molécules d'eau d'hydratation s'éliminant en deux étapes successives: 4 molécules semblent liées plus fortement au cation et leur départ ne s'observe qu'au dessus de 115°. Les dipicolates obtenus à pH 3 correspondent à la formule $\text{Ln}(\text{C}_7\text{H}_3\text{O}_4)_2 \cdot \text{H} \cdot 5 \text{H}_2\text{O}$, les molécules d'eau étant faiblement liées.

On remarque ainsi que, tandis qu'à pH 6 les dipicolates formés pourraient correspondre aux sels normaux d'un diacide avec des cations trivalents, les dipicolates précipités en milieu acide ont une structure différente. Ils se distinguent d'ailleurs des premiers, et des picolates eux-mêmes, par une stabilité thermique (croissante avec le numéro atomique) nettement plus faible; ce fait pourrait correspondre à la possibilité d'existence de liaisons à caractère plus covalent mettant en jeu l'atome d'azote du noyau pyridinique dans un phénomène de chélation. GRENTHE² au cours d'une étude du système acide dipicolique-cations de terres rares en solution aqueuse, a observé la précipitation de produits solides correspondant à la formule $\text{Ln}(\text{dipic})_2 \cdot \text{H}_2\text{O}$, donc de composition semblable aux composés que nous avons précipités à pH 3, mais avec une seule molécule d'eau d'hydratation.

La décomposition thermique de tous les composés étudiés conduit à l'oxyde correspondant, en donnant intermédiairement un dioxymonocarbonate Ln_2O_3 , CO_2 . Pour un même cation, les différents dioxymonocarbonates ont été identifiés par leurs clichés Debye-Scherrer de diffraction R.X. Nous avons noté une exception: les dioxymonocarbonates de praséodyme obtenus par décomposition du picolate et du dipicolate précipité en milieu acide donnent des clichés identiques entre eux, mais différents de celui obtenu pour le produit de décomposition du dipicolate précipité à pH 6. Les raies obtenues étant parfois relativement larges sur un fond continu intense, nous avons recristallisé les produits correspondants en atmosphère de CO_2 à plus haute température en vérifiant que ni la position ni l'intensité relative des raies n'étaient modifiées.

Des carbonates basiques de formule analogue ont été signalés par de nombreux auteurs dans les produits de décomposition des carbonates de terres rares ou des oxalates, notamment par PREISS *et al.*³, BISHOP⁴, et CARO ET LORIERIS⁵.

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¹ G. BLACK, E. DEFF ET B. B. CORSON, *J. Org. Chem.*, 14 (1949) 14.

² I. GRENTHE, *J. Am. Chem. Soc.*, 83 (1961) 360.

³ J. PREISS, R. DUSSIK ET N. RAINER, *Z. Anorg. Chem.*, 131 (1923) 287.

⁴ C. B. BISHOP, *Thèse*, Michigan State University, 1959.

⁵ P. CARO ET J. LORIERIS, *J. Rech. Centre Nat. Rech. Sci.*, 8 (1957) 107.

(Reçu le 11 février, 1963)

A modified method for the titrimetric determination of manganese in ores and metals

We have recently tested various methods for the titrimetric determination of manganese¹ and have proposed a new modification for the reductimetric determination of this element in complexes of the type $Mn[(PO_4)_2]^{3-2,3}$. In the method proposed, the complex of manganese(III) is titrated potentiometrically with iron(II) sulphate or hydroquinone solution. In the practical application of this method, the presence of larger copper concentrations causes the value of the potential change at the equivalence point to become greatly decreased. For this reason, the possibility of employing other reductimetric reagents has been examined and potassium iodide has proved to be the most suitable of the reductants studied. A method for the direct potentiometric titration of manganese(III) with potassium iodide has been developed in which the potential change at the equivalence point is unaffected even by large amounts of copper; if a visual end-point is desired, it is possible to apply an indirect method, in which the iodine liberated after addition of excess of potassium iodide is titrated with thiosulphate. Even a high concentration of iron, as well as large amounts of other common elements, do not interfere in this determination.

EXPERIMENTAL

A 0.1 *M* solution of potassium iodide was prepared from the pure substance (A.R.) and its titre was determined argentimetrically with a silver nitrate solution which had been standardized against pure sodium chloride. A 0.01 *M* solution of iodide was obtained by precise dilution of the 0.1 *M* solution. A 0.1 *M* solution of manganese sulphate was prepared from the pure substance and its titre was checked by titration with EDTA in presence of murexide indicator.

The potentiometric titrations were carried out by means of the Multoscop instrument (Laboratorní potřeby) using a platinum indicating electrode and a calomel reference electrode.

RESULTS AND DISCUSSION

As mentioned in a previous communication³, it is necessary, when manganese is oxidized to the trivalent state in a phosphoric acid medium, to ensure that an excess of potassium ions is present, because the potassium salt of the diphosphatomanganese(III) complex is more stable than the corresponding acid. In the present work, dipotassium hydrogen phosphate was added instead of potassium carbonate³, thus eliminating any possible loss by violent reaction of the solution with carbonate.

The procedure was as follows: 25 ml of concentrated phosphoric acid and 2 g of dipotassium hydrogen phosphate were added to the solution of manganese(II) salt (0.5 to 25 mg Mn) and after dissolution, 0.2 g of potassium bromate added; the mixture was heated slowly and carefully on an asbestos plate. When the bromine vapour had evaporated, the violet solution was cooled and diluted to about 50 ml with distilled water, and titrated with 0.01–0.1 *M* potassium iodide potentiometrically.

The potential stabilised immediately during the titration, but near the equivalence point it was necessary to wait for about 1.5 min between additions. The inflexion potential was approximately 450 mV, the potential change at the equivalence point being about 200 mV for 0.02 ml of 0.1 *M* iodide, or about 100 mV for 0.02 ml of 0.01 *M* iodide. Some results obtained by this method are given in Table I.

TABLE I
TITRATION OF MANGANESE(III) WITH 0.1 *M* IODIDE SOLUTION

<i>Mn</i> taken (mg)	No. of results	Average <i>Mn</i> found (mg)	% Error	
			Maximum	Minimum
27.24	4	27.15	-0.87	-0.07
16.34	3	16.24	-0.91	-0.30
5.45	2	5.49	+0.73	—
2.72 ^a	4	2.715	±0.73	0.0
1.63 ^a	4	1.628	±1.22	0.61
0.54 ^a	2	0.535	-1.85	0.0

^a Titrated with 0.01 *M* iodide.

TABLE II
TITRATION OF MANGANESE(III) IN THE PRESENCE OF IRON AND SOME ANIONS

<i>Mn</i> taken (mg)	<i>Fe</i> present (mg)	<i>Cl</i> - present (mg)	<i>SO</i> ₄ ²⁻ present (mg)	<i>Mn</i> found (mg)	Error (%)
16.34	—	163 ^b	—	13.74	-15.9
16.34	—	1630 ^b	—	12.19	-25.0
16.34	—	—	163 ^c	16.13	-1.28
16.34	—	—	1630 ^c	16.02	-1.95
27.24	27	51.3	—	27.33	+0.33
5.45	54	102.5	—	5.04	-7.52
2.72	27	51.3	—	2.76	+1.47
5.45	545	1025	—	7.03	+28.5
2.72	272	513	—	2.88	+5.88
16.34	163	—	420.5	15.80	-3.30
16.34	408	—	665	15.23	-6.79
16.34	817	—	1331.7	15.80	-3.30
16.34	1630	—	4205	15.89	-2.75
16.34 ^a	160	—	—	16.35	+0.10 ^d
16.34 ^a	320	—	—	16.02	-2.06 ^d
16.34 ^a	650	—	—	16.24	-0.81 ^d
16.34 ^a	980	—	—	16.02	-1.84 ^d
16.34	1300	—	—	16.46	+0.73 ^d

^a Dissolved in HClO₄

^b HCl

^c H₂SO₄

^d Error % Mn in Fe

For practical application it was necessary to study the effect of iron, and to find out whether copper caused a decrease in the potential change at the equivalence point, as it did in titrations with iron(II) sulphate or hydroquinone. A study of the effect of anions, arising from the acid used to dissolve the sample, *i.e.* chloride, sulphate and perchlorate, showed that chloride caused errors in the results, as did unduly large amounts of sulphate. The best results in the titration of manganese in the presence of iron were obtained in perchlorate media, *i.e.* when perchloric acid was employed to dissolve the sample (Table II).

The fact that iron(III) was not reduced by potassium iodide is caused by the redox potential of the Fe(II)/Fe(III) system being shifted in the medium mentioned towards a value of about 0.4 V, so that a sufficient potential difference was not achieved to allow reaction with iodide⁴. Even an 80-fold excess of iron did not interfere in the determination. Moreover, the potential change at the equivalence point was the same as that obtained in the titration of solutions containing manganese(III) salts only. Similar observations were made for the titration of manganese in the presence of copper (Mn:Cu=1:50).

For practical purposes, an indirect titration was suitable, in which excess of potassium iodide was added to the dissolved sample after conversion of manganese to a manganese(III) complex; the equivalent amount of iodine liberated was then titrated with thiosulphate solution in presence of starch indicator.

Recommended procedure

The method of decomposition is selected according to the type of sample. For ferromanganese or fluxes, dissolve the sample containing about 15 mg of manganese by heating with 10 ml of about 70% perchloric acid, evaporate the solution and dissolve the residue in 20 ml of concentrated phosphoric acid. For manganese ores,

TABLE III
DETERMINATION OF MANGANESE IN SOME SAMPLES

<i>Sample</i>	<i>% Mn</i>	<i>% Mn found</i>	<i>% Error</i>
Ferromanganese ^a	77.70	77.10	-0.77
Flux b: VUS-2B ^b	16.26	15.74	-3.25
Flux VUS ^c	26.70	26.91	+0.78
Ore standard (USSR origin) ^d	52.58	53.00	+0.80
Bronze ^e	1.32	1.33	+0.75

Percentage compositions:

- ^a C, 6.69; Si, 0.46; Cu, 0.11; Ni, 0.10.
- ^b SiO₂, 22; Fe₂O₃, 0.50; Al₂O₃, 23; CaO, 3.90; CaF₂, 25; MgO, 0.2; (Na₂O + K₂O), 3; MnO, 21.
- ^c SiO₂, 43.5; Fe₂O₃, 0.30; Al₂O₃, 4.90; CaO, 5.50; MgO, 6.50; CaF₂, 3.20; MnO, 3.20.
- ^d 52.58 Mn.
- ^e Sn, 0.30; Cu, 83.37; Pb, 0.19; Ni, 3.11; Fe, 0.40; Al, 10.95; P, 0.097; Si, 0.12; Sb, 0.011; ZnO, 0.05; As (0.02).

dissolve about 0.25 g in 10 ml of concentrated sulphuric acid and 5 ml of 30% hydrogen peroxide by gentle heating; dilute to a given volume, evaporate an aliquot to a volume of about 2.5 ml, and dilute with 20 ml of concentrated phosphoric acid.

For manganese bronze, carefully dissolve about 0.5 g in 15 ml of concentrated nitric acid, evaporate the solution to dryness, and dissolve the residue with 20 ml of concentrated phosphoric acid. The further procedure was the same as that described above for solutions containing the pure manganese salt. Typical results are given in Table III.

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¹ J. DOLEŽAL AND J. ZÝKA, *Chem. Listy*, 10 (1958) 369.

² C. O. INGAMILLS AND W. S. BRADSHAW, *Chemist-Analyst*, 47 (1958) 11.

³ J. DOLEŽAL, I. KLUH AND J. ZÝKA, *Z. Anal. Chem.*, 177 (1960) 14.

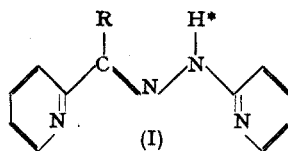
⁴ G. GOPALA RAO AND SAGI SEETARAMA RAJU, *Talanta*, 9 (1962) 715.

(Received February 6th, 1963)

Anal. Chim. Acta, 29 (1963) 70-73

Analytical possibilities of a series of new aromatic-type chelate compounds

Recently LIONS AND MARTIN¹ and GELDARD AND LIONS² reported a series of cationic complexes, the tridentate ligands of which were of the type (I).



In alkaline solution, these chelate compounds were found to lose a proton (marked H* in (I)) from each ligand, usually forming neutral complexes soluble in a variety of organic solvents. Moreover, as some of the complexes were highly coloured in one or both forms, it was suggested that they had analytical possibilities. In order to evaluate these possibilities, the present authors have carried out a survey of the visible spectra of a number of metal ions in the presence of 1,3-bis(2'-pyridyl)-1,2-diazaprop-2-ene (I, R=H).

Apparatus

Spectra were measured with a Perkin-Elmer Spectracord, Model 4000. pH values were determined with a Radiometer pH Meter 4.

Anal. Chim. Acta, 29 (1963) 73-75

Reagents

A.R. quality reagents were used wherever possible. Solutions for test contained 10 μg of the metal per ml.

Solutions of 1,3-bis(2'-pyridyl)-1,2-diazaprop-2-ene were prepared by dissolving the compound in ethyl alcohol (5 ml) and diluting to 250 ml with distilled water.

Acid buffer solution was prepared from glacial acetic acid (40 ml) and sodium acetate trihydrate (40 g) diluted to 1 l with water.

Alkaline buffer solution was prepared from concentrated aqueous ammonia (sp. gr. = 0.90, 36 ml) and ammonium chloride (12 g) diluted to 1 l with water.

Procedure

To a 50-ml volumetric flask were added: (a) 10 ml of the metal test solution; (b) 20 ml of the freshly prepared ligand solution, containing sufficient ligand to give a final molar concentration two to four times that of the metal ion; (c) 1 M sodium hydroxide until the solution was approximately neutral; and (d) 5 ml of the acid or alkaline buffer solution. The mixture was then made up to the mark with water and the visible spectrum and pH measured.

Results

The following metals were tested:

Mg(II), Ca(II), Sr(II), Ba(II), Al(III), La(III), Ce(IV), U(VI), Ti(IV), Zr(IV), V(IV), Cr(III), Mo(VI), W(VI), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Ru(III), Rh(III), Pd(II), Os(IV), Ir(IV), Pt(II), Pt(IV), Cu(II), Ag(I), Au(III), Zn(II), Cd(II), Hg(II), In(III), Tl(I), Sn(II), Sn(IV), Pb(II), As(III), Sb(III) and Bi(III).

Those metals whose complexes showed definite absorption peaks in the wavelength range 360 to 700 $m\mu$ and appeared to have analytical application are shown in Table I.

TABLE I
ABSORPTION PEAKS OF METAL COMPLEXES

<i>Metal</i>	<i>pH</i>	λ_{max} ($m\mu$) of absorption peak	<i>Optical</i> <i>density</i> at λ_{max}	<i>Observed</i> <i>colour</i>
Co(II)	4.3	468	0.95	Orange
	9.8	467	0.9	Orange
Ni(II)	4.3	—	—	Pale yellow*
	9.7	431	1.4	Green-yellow
Zn(II)	4.3	—	—	Pale yellow*
	9.7	430	0.8	Green-yellow
Cu(II)	4.3	—	—	Pale yellow*
	9.7	452	0.6	Yellow
Pd(II)	4.3	508	0.2	Red
	9.6	508	0.1	Red
Cd(II)	4.3	—	—	Pale yellow*
	9.6	433	0.15	Yellow
Fe(II)	4.1	518	0.25	Orange-red
	9.5	569	0.15	Brown-yellow

* Solutions of the ligand alone were pale yellow at all the quoted pH values.

The iron(III) solution at pH 4.2 changed, on standing, from an initial pale yellow to an orange-red colour which essentially reached maximum intensity after 30 min. The spectrum then resembled that obtained for the iron(II) solution at a similar pH. This system is at present being studied in greater detail.

It is evident from Table I that in most cases the solutions show a markedly different absorption at the two pH values quoted. Consequently, these complexes should be useful as acid-base indicators. In addition, an extractive method of end-point detection could be applicable where the alkaline form is uncharged and soluble in organic solvents.

The observed colour intensities of some of the solutions in Table I are high, especially in view of the fact that the metal concentration is only 2 μg per ml in all cases. These complexes should therefore be useful for the colorimetric estimation and qualitative detection of the metals concerned.

Work is proceeding on the above analytical applications of this new series of chelate compounds, and will be the subject of further publications.

We wish to thank GELDARD AND LIONS for permission to carry out this work and for gifts of 1,3-bis(2'-pyridyl)-1,2-diazaprop-2-ene.

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¹ F. LIONS AND K. V. MARTIN, *J. Am. Chem. Soc.*, 80 (1958) 3858.

² J. F. GELDARD AND F. LIONS, *J. Am. Chem. Soc.*, 84 (1962) 2262.

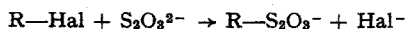
(Received January 10th, 1963)

Anal. Chim. Acta, 29 (1963) 73-75

Determination of some organic halides by formation of Bunte salts with thiosulphate and iodimetry

Organic halides are usually determined by methods depending on acid or alkaline hydrolysis; this converts the organically bound halogen to halide ion which can then be determined, generally by titrimetric (direct and indirect), gravimetric or turbidimetric determinations using silver(I) or mercury(II) reagents. Alternatively, a measured excess of alkali reagent may be used and the excess back-titrated with acid.

The reaction of halides with thiosulphate has been known for many years, the original publication¹ dating from 1874. The so-called Bunte salts are formed according to the reaction:

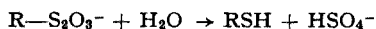


Extensive kinetic studies of the reaction have been made (references 2 to 10 are a selection), mostly concerning the influence of solvent (dielectric constant), salts and other components on the reaction rate. They have been restricted almost entirely to the reactions of alkyl halides and bromoacetate and other halogen-substituted acids and esters.

Anal. Chim. Acta, 29 (1963) 75-78

The reactions appears in many cases to be comparatively fast; the thiosulphate reagent is mild in comparison to acids and alkalis and the back-titration of unreacted thiosulphate with iodine is capable of high accuracy. An attempt was therefore made to adapt the reaction to the determination of at least certain halides.

The principal possible side-reactions are decomposition of the thiosulphate reagent and of the Bunte salt, and reaction of the halide with the solvent. In approximately neutral solution, thiosulphate is reasonably stable and tests demonstrated that 0.1 *N* solutions of sodium thiosulphate at pH 4 to 10 could be heated for over 4 h at temperatures up to 90° without measurable loss in titre. The Bunte salts may hydrolyse at higher temperatures, yielding mercaptans and hydrogen sulphate⁷:



However, this decomposition appears to be slow and, although during the present work odours presumably attributable to mercaptans were sometimes noted, the quantitative data were negligibly affected. Lastly, only in very few cases was hydrolysis of the halides a serious competing reaction.

Experimental

Halides. These were purified by distillation or crystallisation. The purity of aliphatic halides was tested gas chromatographically and that of halogen-containing acids by titration with standard alkali.

Solutions. The halides were mostly used in dioxane solution; the dioxane was purified by removal of peroxides and distillation. Acetone and lower alcohols were used in a few instances.

Sodium thiosulphate, 0.1 *N*, was prepared in freshly distilled and boiled water but no stabilising addition, *e.g.* of carbonate, was made.

Procedure. Measured volumes of halide and thiosulphate solutions were mixed and maintained for various times at temperatures ranging from 10° to 60°. The solvent composition was adjusted to *ca.* 1:1 organic solvent: water. The amount of thiosulphate ranged from 3 to 5 times the theoretical amount in most cases. Halogen-containing acids were first titrated with alkali to phenolphthalein. At the end of the chosen reaction times, the solutions were titrated with iodine solution which had been standardised with arsenite. The end-point determination was usually visual (the yellow colour of iodine itself or a starch indicator).

Results

Table I show some typical results, expressed as the extent of reaction after various times.

Halogen-substituted carboxylic acid salts, esters and ketones, and some alkyl and aralkyl halides were found to react quantitatively under the conditions used, at moderate to high speeds. With allyl chloride and bromide, it proved impossible to obtain more than 94% conversion, a value which was uninfluenced by the excess of thiosulphate, the solvent composition (more or less water, or replacement of dioxane by acetone), variation of temperature between 10 and 60°, and by prolonged reaction times. Methyl bromide is known to undergo only about 90% conversion¹¹ and on the basis of kinetic studies¹², this was suggested as being caused by a competing reaction yielding a product which reacted with iodine (*e.g.* CHO₃SO₂S⁻). Pos-

TABLE I
REACTION OF HALIDES WITH THIOSULPHATE (AT 60°)

Halide	Approx. excess of thiosulphate (<i>x</i> -fold)	Percentage conversion					
		Reaction time (min)					
		5	10	20	40	60	120 240
Ethyl iodide	3	58.3	78.9	92.9	99.2	99.6	99.9
Propyl iodide	5		43.4	57.8	76.1	83.0	95.0 99.2
Isopropyl iodide	5		12.1	15.4	26.0	33.0	51.5 69.6
Propyl bromide	2.5	17.0			66.1	75.5	84.0 89.0
Allyl bromide	3.5	94.7	93.9 (average of 7 values)				
2, 4-Dinitrochlorobenzene	10		17.7	30.7	43.9	51.5	
Benzyl chloride	3.5	50.5	78.7	89.1	97.8	99.9	
<i>p</i> -Nitrobenzylchloride	5		89.2	98.9	99.7		
Bromoacetate	3	68.9	94.9	100.2 (average of 8 values, ranging from 99.6 to 100.9)			
Chloracetate	2.5		10.4	18.9	29.2	35.5	50.9 60.0
Ethyl bromoacetate	6	95.6	99.4	100.2			
Bromoacetone	5	100.2	100.3				
ω -chloroacetophenone (50°)	3.5	98.2	99.7 (average of 9 values)				

sibly the same explanation may be valid for the allyl halides. Impurities in the two halides were shown gas chromatographically not to exceed about 0.5%.

Aromatic sulphonyl chlorides, on the other hand, reacted with about 1.6 moles of thiosulphate, which may indicate a competing reaction such as:

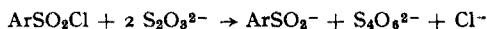


TABLE II

TIMES FOR ESSENTIALLY COMPLETE REACTION OF VARIOUS HALIDES*

Halide	Temp. (°)	Time (min)
Methyl iodide	25	50-60
Ethyl iodide	50	110-120
Ethyl iodide	60	60-70
<i>n</i> -Propyl iodide	60	300-360
Benzyl chloride	60	60
<i>p</i> -Nitrobenzyl chloride	60	30-35
α -Chloromethylnaphthalene	25	350-400
α -Chloromethylnaphthalene	60	30
Bromoacetate (sodium salt)	60	20
β -Bromopropionate (sodium salt)	60	50
Chloroacetone	60	5-8
Bromoacetone	60	2-3
ω -chloroacetophenone	50	10
ω -bromoacetophenone	40	6-8
Ethyl α -bromopropionate (DL form)	60	30-35
Ethyl chloroacetate	60	30
Ethyl bromoacetate	60	15
Methyl bromoacetate	60	3-5
Ethyl iodoacetate	60	2-3

* A 3-5-fold excess of thiosulphate was used.

The reaction was fairly fast and it is hoped to investigate this further. Dihalides like dibromoethane and 1,3-dibromopropane reacted impracticably slowly. In contrast to the statement of SLATOR², however, both bromide atoms of the former compound seemed to react and not just a single atom. Polyhalides like chloroform and carbon tetrachloride underwent very little reaction.

In certain cases, such as trityl chloride and carboxylic acid chlorides, the hydrolysis reaction with water was evidently far faster than that with thiosulphate so that low results were consistently obtained.

The halides which reacted quantitatively are listed in Table II, where the appropriate conditions of temperature and time are given. All of these halides and related compounds could then be determined by this relatively mild and simple method. It might be possible to accelerate the reaction by using temperatures higher than the 60° arbitrarily chosen for the present work (most of the halides studied have boiling points well above 60°), by addition of catalysts (*e.g.* LaCl₃ for halocarboxylate salts⁸) or by change of solvent (a lower dielectric constant accelerates the reaction of alkyl halides⁵). This would extend the range of applicability of the method.

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- ¹ H. BUNTE, *Chem. Ber.*, 7 (1874) 646.
- ² A. SLATOR, *J. Chem. Soc.*, 85 (1904) 1286; 87 (1905) 481.
- ³ A. SLATOR AND D. F. TWISS, *J. Chem. Soc.*, 95 (1909) 93.
- ⁴ V. K. LAMER AND M. E. KAMNER, *J. Am. Chem. Soc.*, 53 (1931) 2832; 57 (1935) 2662, 2669.
- ⁵ D. STRAUP AND E. J. COHN, *J. Am. Chem. Soc.*, 57 (1935) 1794.
- ⁶ L. FILIPCZYK, *Roczniki Chem.*, 18 (1938) 36, 117.
- ⁷ T. I. CROWELL AND L. P. HAMMETT, *J. Am. Chem. Soc.*, 70 (1948) 3444.
- ⁸ F. G. CIAPETTA AND H. M. TOMLINSON, *J. Phys. and Colloid Chem.*, 55 (1951) 429.
- ⁹ W. J. BROACH AND E. S. AMIS, *J. Chem. Phys.*, 22 (1954) 39.
- ¹⁰ G. CORSARO AND M. C. MORRIS, *J. Electrochem. Soc.*, 108 (1961) 689.
- ¹¹ E. A. MOELWYN-HUGHES, *Trans. Faraday Soc.*, 37 (1941) 279.
- ¹² P. M. DUNBAR AND L. S. HAMMETT, *J. Am. Chem. Soc.*, 72 (1950) 109.

(Received February 25th, 1963)

Infrared spectrophotometry of aqueous nitrate, nitrite and sulfate solutions

Microgram quantities of inorganic nitrate, nitrite, and sulfate have been determined with good accuracy and selectivity by infrared measurements of potassium bromide discs in which these ions were incorporated¹⁻³. The disc materials were prepared by freeze-drying aqueous solutions, a process which yielded uniform and finely-divided dispersions of the samples in the matrix material and served to couple the infrared determinations with prior chromatographic separation and concentration steps. To permit a fuller evaluation of the applicability of infrared spectrophotometry to inorganic analytical problems, a largely neglected field, it is desirable to report briefly some results of direct measurements on aqueous solutions.

Water is not normally considered a good infrared solvent, but it has been used occasionally, beginning with COBLENTZ in 1905⁴. GORE *et al.*⁵ and BLOUT AND LENORMONT⁶, among others, recorded spectra through most of the rock salt region by using heavy water in the portions where water itself is opaque. PLYLER AND ACQUISTA⁷ pointed out that water transmitted sufficiently from about 6.5 to 10 μ to permit quantitative measurements of aqueous solutions, and POTTS AND WRIGHT⁸ showed that certain water-soluble organic compounds could be determined by measurements in this region. STERNGLANZ has discussed the use of water as an infrared solvent⁹, and GOULDEN has pointed out that this is occasionally advantageous¹⁰. DUVAL¹¹ has used the infrared spectrum of a drop of aqueous solution to identify various inorganic anions. The spectra of sulfate, sulfite, thiosulfate, and tetrathionate in aqueous solution have been recorded by ANTIKAINEN¹². It is now very convenient to obtain infrared spectra of aqueous solutions in cells with windows of Irtran-2, a relatively new infrared-transmitting material, because of its insolubility in water and other desirable properties¹³.

In the previous work with potassium bromide discs, microgram quantities of nitrate, nitrite, and sulfate were dispersed in 300 mg of potassium bromide to give reasonable absorbance readings. The thickness of the discs was about 0.75 mm. Still greater sensitivity could have been attained by means of micro discs in which a much greater fraction of the sample was in the beam. With aqueous solutions, on the other hand, much smaller path lengths must be used. Then, although the total quantity of sample in the beam may still be very small, the sensitivity in terms of concentration is much lower. Thus the measurements reported here involve solutions containing, not microgram, but milligram quantities per ml.

An additional adverse effect upon sensitivity is created by the broadening of the absorption bands in aqueous solution as compared with potassium bromide discs. This may be partially countered by replotting the spectra on a scale linear in frequency and measuring areas under the absorption bands, but this is not generally convenient. Thus it is suggested here that the infrared measurements of aqueous solutions extend upward the useful range as previously reported and may be of interest to analysts dealing with milligram quantities of these ions.

Apparatus and reagents

Infrared spectra were recorded with a Perkin-Elmer Model 137 'Infracord' spectrophotometer with rock salt optics. Solutions were measured in cells with Irtran-2 windows obtained from the Connecticut Instrument Corp., Wilton, Conn. The path length through the sample cell was 0.0119 mm as determined in the usual manner by means of interference fringes. Solutions were prepared with ordinary distilled water and reagent grade chemicals.

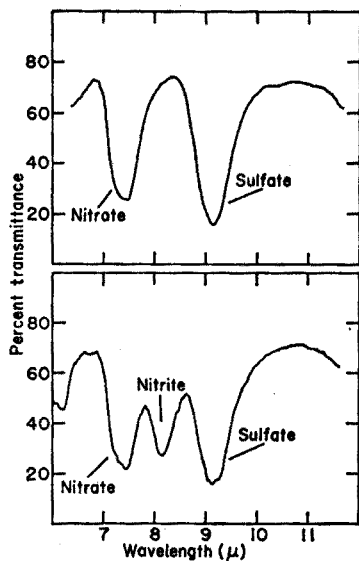


Fig. 1. Spectra of nitrate-sulfate and nitrate-nitrite-sulfate mixtures: aqueous solutions of potassium salts containing 40 mg per ml of each anion.

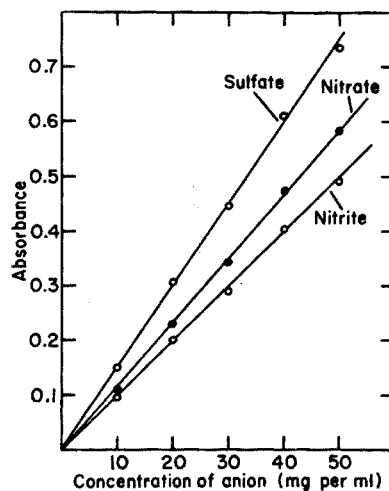


Fig. 2. Calibration curves for sulfate, nitrate and nitrite in aqueous solution.

Spectra

Fig. 1 shows the spectra of a nitrate-sulfate mixture and a nitrate-nitrite-sulfate mixture. The extent to which the absorption bands overlap may be judged from the figure; measurements at the wavelengths of maximum absorption are practically free of interferences among the three ions. Comparison may be made with Fig. 2 of reference 3 to see the difference in the sharpness of the bands in potassium bromide discs and in aqueous solution.

Calibration curves

Fig. 2 shows typical calibration curves for the three ions. It may be seen that Beer's law is followed over a useful absorbance range. The same base-line, drawn to connect transmittances at about 6.7 and 10.8 μ , was used to calculate absorbance values for the three ions.

Reproducibility

A series of ten pure potassium sulfate solutions containing from 10 to 50 mg of

sulfate per ml, was analyzed. The average relative deviation of the infrared results from the known concentrations was 3%. Relative errors of about the same magnitude were found with pure solutions of potassium nitrate and of potassium nitrite.

Interferences

The presence of nitrate at a level of 50 mg per ml did not increase the error in the sulfate determination, nor did sulfate affect the nitrate measurement adversely. Similarly, nitrite caused no additional error in sulfate or nitrate measurements. On the other hand, there was a slight contribution by both nitrate and sulfate to the absorbance at the nitrite wavelength. When these two ions were both present at concentrations of 50 mg per ml, absorbance values for 50 mg per ml of nitrite were about 7% too high. The safest procedure in unknown situations is to solve simultaneous equations for the absorbances at the three wavelengths to obtain the concentrations of the three anions.

In previous studies with potassium bromide discs, it was found that the shape of the sulfate band and the absorbance values were dependent upon the nature of the cation accompanying the sulfate¹. This cation dependence was not observed with nitrite and nitrate. With aqueous solutions, the sulfate band became cation-independent: potassium, sodium, lithium, zinc, and cadmium sulfates yielded identical spectra, and the absorbance values depended only on the sulfate concentration.

Most organic compounds exhibit absorption bands in the 7 to 10 μ region and interfere in the determination of nitrate, nitrite, and sulfate. Common inorganic interferences are borates, carbonates, phosphates, perchlorates, and ammonium salts, all of which absorb strongly in this region of the spectrum.

As a result of this work and related studies, it is concluded that infrared spectrophotometry of aqueous solutions of inorganic ions will be of rather limited value to analytical chemists. The accuracy, sensitivity, and selectivity are not highly attractive. However, it is possible that such measurements may be useful for certain special applications.

The authors gratefully acknowledge the support of this work by the U. S. Atomic Energy Commission through Research Contract No. AT-(40-1)-2046.

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¹ H. TAI AND A. L. UNDERWOOD, *Anal. Chem.*, 29 (1957) 1430.

² I. CITRON AND A. L. UNDERWOOD, *Anal. Chim. Acta*, 22 (1960) 338.

³ I. CITRON, H. TAI, R. A. DAY, JR. AND A. L. UNDERWOOD, *Talanta*, 8 (1961) 798.

⁴ W. W. COBLENTZ, *Investigations of Infrared Spectra*, Carnegie Institution of Washington, Washington, D.C., 1905, p. 56.

⁵ R. C. GORE, R. B. BARNES AND E. PETERSEN, *Anal. Chem.*, 21 (1949) 382.

⁶ E. R. BLOUT AND W. LENORMONT, *J. Opt. Soc. Am.*, 43 (1953) 1093.

⁷ E. K. PLYLER AND N. ACQUISTA, *J. Opt. Soc. Am.*, 44 (1954) 505.

⁸ W. J. POTTS, JR. AND N. WRIGHT, *Anal. Chem.*, 28 (1956) 1255.

⁹ H. STERNGLANZ, *Appl. Spectry*, 10 (1956) 77.

¹⁰ J. D. S. GOULDEN, *Spectrochim. Acta*, (1959) 657.

¹¹ C. DUVAL, *Mikrochim. Acta*, (1956) 741.

¹² P. J. ANTIKAINEN, *Suomen Kemistilehti*, 31B (1958) 223; *C. A.*, 52 (1958) 17958.

¹³ *C. I. C. Newsletter No. 9*, Connecticut Instruments Corp., Wilton, Conn., Sept. 1960.

(Received January 22nd, 1963)

Determination of traces of copper

When traces of copper (0.5 to 20 p.p.m.) were determined in carbon black by burning off the material, treating the ash with nitric acid and sulphuric acid, and determining copper colorimetrically as copper diethyldithiocarbamate, rather large variations were obtained in the results of replicate analyses. In general, such variations were not found with determinations of copper in other materials which need a preliminary ashing, *viz.* raw and vulcanised rubber, etc., or in products which do not need ashing, *e.g.* mineral fillers. Therefore, the colorimetric method was checked by means of an entirely different procedure, *viz.* radiochemically.

For the radiochemical procedure, the carbon black, after irradiation in a thermal neutron flux, was digested with sulphuric acid and then oxidized with a mixture of perchloric acid and nitric acid; the copper was extracted with sodium diethyldithiocarbamate after which the radiation activity of the copper was measured with a γ -spectrometer. This procedure gave results which were notably lower (5 to 10 times smaller) than those obtained by the colorimetric method. On the other hand, both methods generally gave very similar results for some rubber vulcanisates.

Investigations showed that the porcelain crucibles in which the ashing was performed, appeared to be the cause of the differences in results for the samples of carbon black. When silica crucibles were used, the results of the colorimetric and radiochemical methods were in good agreement with each other. It is therefore necessary to compare the performance of both methods applied to other materials, and such investigations are in progress.

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(Received February 26th, 1963)

Anal. Chim. Acta, 29 (1963) 82

Titrimetric determination of iron(III) with titanium(III) at room temperature

Safranine T, phenosafranine and neutral red as indicators

When methylene blue is used as indicator in the titration of iron(III) with titanium(III) solution, as originally prescribed by MONNIER¹, the end-points are not quite satisfactory even in presence of salicylic acid, as suggested by LAUTERBAUCH². This observation appears to be the general experience; KOLTHOFF AND BELCHER³ state that if methylene blue is used at room temperature the results are about 2% high and that accurate values are obtained only at 50–70°. KOLTHOFF⁴ found that an excess of 1–2% of titanous solution is required when thiocyanate is used as the indicator at room temperature. In view of the unsatisfactory behaviour of these

Anal. Chim. Acta, 29 (1963) 82–84

indicators, we have examined safranin T, phenosafranin and neutral red as indicators in this titration. These dyes have already been employed as indicators for the titration at 60° of antimony(V) with titanous sulphate solution⁵ and for the titration of titanium(III) with sodium metavanadate at room temperature⁶. We have shown that these dyes also function very satisfactorily in the titration of iron(III) with titanium(III), provided that oxalic acid is present to catalyse the indicator reaction.

Reagents

Titanous chloride solution. A 0.05 *N* solution was prepared by suitably diluting a 13.6% A.R. solution (May & Baker, London) with 2.0 *N* hydrochloric acid. The solution was found to be free from iron(II). The diluted solution was stored under carbon dioxide; it was standardised by running an aliquot into an excess of 0.1 *N* iron(III) solution, and titrating the resulting iron(II) with a standard solution of potassium dichromate with barium diphenylamine sulphonate as indicator.

Ferric alum solution. An approximately 0.1 *N* solution was prepared from G.R. grade ferric ammonium sulphate (E. Merck, Darmstadt) and standardised by the usual procedure.

Indicator solutions. Aqueous 0.1% solutions of each indicator were prepared from samples (T. Gurr & Co.) for use as biological stains. In 1.0 *N* hydrochloric acid, the colours of safranin T, phenosafranin and neutral red were red, reddish purple and purple, respectively. Fresh solutions of the indicators should be used; aged samples were unsatisfactory for use as indicators.

All other chemicals used were of analytical reagent quality.

Recommended procedure

The titrations were carried out in a 150-ml Pyrex titration flask fitted with a 3-holed ebonite lid, through which passed a microburette and inlet and outlet tubes for carbon dioxide.

For a titration, mix 25 ml of 3.0 *N* hydrochloric acid, 15–20 ml of 0.5 *M* oxalic acid, the iron(III) solution and 0.2 ml of the indicator solution and dilute to 75 ml. Pass a steady rapid stream of carbon dioxide through the mixture for about 10 min. Maintaining the gas flow, titrate rapidly with titanium(III) solution until the brown colour becomes purple; then titrate dropwise until the purple colour completely disappears. The end-points were quite sharp, but the colour changes were irreversible. Magnetic stirring was used, although the agitation provided by the gas stream was really sufficient.

Results and discussion

The results of a large number of titrations over the range 0.4–1 millimole of iron(III) showed that the accuracy of the method is ± 0.3 –0.5%.

In initial tests of the indicator action, 75 ml of 1.0 *N* hydrochloric acid containing 0.2 ml of the indicator solution were deaerated with carbon dioxide and 0.05 ml of about 0.05 *N* titanium(III) chloride solution was added with stirring; the time taken for the discharge of the indicator colour was noted. The reduction of all three dyes by titanium(III) was slow at room temperature but was markedly accelerated by oxalic acid, the rate increasing with increasing concentrations of oxalic acid. When 0.1 *M* oxalic acid was present, the dyes were instantaneously reduced by titanium(III).

The transition potentials of the three indicators are + 0.17 V, + 0.16 V and + 0.10 V for safranine T, phenosafranine and neutral red respectively⁶; these values correspond to the potentials at which the colour is discharged in 1.0 N hydrochloric acid solutions containing oxalic acid under carbon dioxide at 28°.

The indicators reported have the following advantages over methylene blue. Under the conditions prescribed, it is not necessary to wait for 2–3 sec after each addition of titrant near the end-point. Methylene blue indicator must be added in quantities just sufficient to colour the solution blue, because of the large indicator correction. The dyes recommended above have much better tinctorial properties so that a brilliant colour can be obtained without an indicator correction being needed. Finally, the colour changes are quite sharp even at room temperature, whereas methylene blue requires a temperature of 50–70°.

One of us (P.V.K.R.) thanks the Council of Scientific and Industrial Research, India, for the award of a Junior Research Fellowship.

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¹ A. MONNIER, *Ann. Chim. Anal. Appl.*, 21 (1916) 109.

² LAUTERBACH, *Ber. 7ten. Intern. verg. chem.-kol.*, 1922, p. 33.

³ I. M. KOLTHOFF AND R. BELCHER, *Volumetric Analysis*, Vol. III, Interscience, New York, 1957, 614.

⁴ I. M. KOLTHOFF, *Rec. Trav. Chim.*, 43 (1924) 816.

⁵ H. HOLNESS AND G. CORNISH, *Analyst*, 67 (1942) 221.

⁶ B. V. S. R. MURTY AND G. GOPALA RAO, *Talanta*, 8 (1961) 438.

(Received November 5th, 1962)

Anal. Chim. Acta, 29 (1963) 82–84

Complex formation and fluorescence Part III. Salicylate complexes

It is possible to determine salicylates in low concentration by the measurement of fluorescence intensity^{1,2}. This is usually carried out between pH 6 and 8 using the fluorescence of the singly charged salicylate anion. There have been only three investigations of the effect of the presence of cations on the intensity of this fluorescence. GOTO³ has reported that iron(III) causes complete extinction of fluorescence. ZITTLE *et al.* and also ROSEN AND WILLIAMS⁵ have shown that at a pH of 10, the presence of magnesium(II) causes a shift in the peak of the fluorescence emission spectrum from that due to the singly charged salicylate anion (410 m μ) to that of the doubly charged anion (390 m μ), with an accompanying increase in intensity of fluorescence.

The writer has investigated the effect of adding cations to salicylate solutions over the pH range 2 to 7. The cations were chosen in order to study several variables: ion size, ion charge and the difference between transition metals and non-transition

Anal. Chim. Acta, 29 (1963) 84–87

metals. Ions used were Cu(II), Co(II), Ni(II), Zn(II), Mg(II), Be(II), Fe(III) and Al(III).

Analytical method

Solutions for fluorescence measurements of bivalent cations were prepared by dilution of solutions in which the ratio of cation to salicylate was 1 to 2. In the case of Fe(III) and Al(III) solutions the effect of a small concentration relative to that of salicylate was desired, since GOTO³ had reported that very small amounts of Fe(III) would completely destroy the salicylate fluorescence. Al(III) was chosen for comparison with Fe(III). Salts used were of reagent grade, and the salicylic acid was obtained from the Eastman Kodak Co. The pH was adjusted before dilution of the solutions, using dilute hydrochloric acid or sodium hydroxide, and was checked after dilution using a Beckman pH meter. All fluorescence measurements were made on the Farrand spectrofluorimeter previously described⁶. The excitation wavelength was set at 610 m μ and a complete emission spectrum was determined for each solution between 330 m μ and 550 m μ .

DISCUSSION OF RESULTS

Of the ions studied only Cu(II), Be(II), Fe(III) and Al(III) caused any change in the fluorescence, either with regard to intensity of fluorescence or range of emission spectrum. Results for Cu(II) and Be(II) are shown in Fig. 1. The effect of small amounts of Fe(III) and Al(III) on the fluorescence intensity of salicylate solutions is shown in Fig. 2. The solutions containing Fe(III) changed on standing. The results in Fig. 2 were obtained immediately after the solutions were prepared. GOTO³ found that the fluorescence of salicylate solutions was destroyed by 2.5 μ g of Fe(III) with no mention being given of relative amounts or concentrations.

As can be seen from Fig. 1, the presence of Cu(II) produced a decrease in fluores-

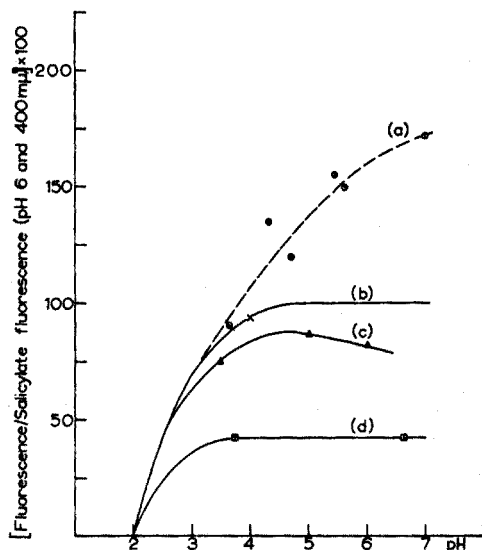


Fig. 1. Effect of pH, Be(II) and Cu(II) on salicylate fluorescence intensity. (a) Be + HSal⁻ (380 m μ); (b) HSal⁻ (400 m μ); (c) Cu + HSal⁻ (400 m μ); (d) HSal⁻ (380 m μ).

cence intensity of salicylate solutions, the decrease becoming greater as the pH increased. This is of particular interest in biological analyses, since SCHUBERT⁷ has stated that there is some connection between the physiological action of salicylates and the presence of copper.

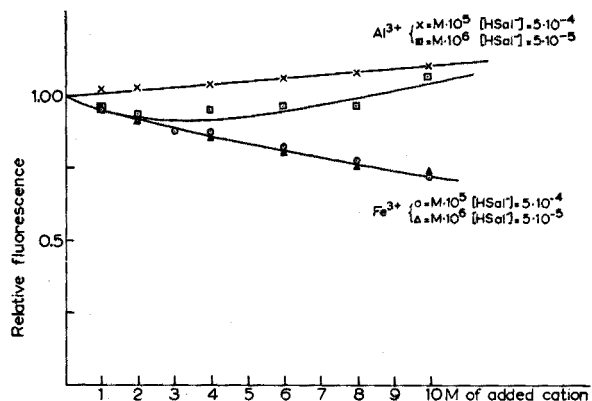


Fig. 2. Effect of Fe(III) and Al(III) on salicylate fluorescence in acetate buffer pH 4.8.

In the case of Be(II), there was not only a pronounced increase in fluorescence intensity, but also a shift of the emission spectrum so that the peak occurred at $380 \text{ m}\mu$, shifting from the $500 \text{ m}\mu$ of the sodium salicylate solutions. (It should be noted that the emission curve is very flat at the "peak", but the shift is quite definite.) This shift did not take place with other solutions. A similar shift reported for solutions of sodium salicylate containing Mg(II) at a pH of 10^{4,5}, has been explained as being due to the formation of a complex ion in which both hydrogens of the salicylate have been displaced, producing the fluorescence spectrum and intensity to be expected for the doubly charged salicylate anion. This anion does not form in sodium salicylate solutions below a pH of 14^{1,2}. The intensity of the fluorescence of the Be(II) complexes was approximately 1.7 times that of the salicylate anion at a pH of 7 measured at $400 \text{ m}\mu$, and almost 4 times that of salicylate ion at pH 7 at $380 \text{ m}\mu$.

HEITNER-IRGUN AND COHEN⁸ concluded from investigations of the Cu(II)-salicylate system by spectrophotometric methods that it is not possible to decide whether the ML_2 complex is one in which the phenolic hydrogen has been displaced, and suggested that there may be a mixture present. The beryllium complex reported by SCHUBERT AND LINDENBAUM⁹ is an MHL type, in which the phenolic hydrogen has not been displaced. The emission spectra obtained in the present work indicate that the beryllium complex is of the ML_2 type in which both hydrogens of the salicylic acid have been displaced. Since the copper complex does not fluoresce, no direct evidence is obtained with regard to the problem set out by HEITNER-IRGUN AND COHEN. It may be possible to obtain the answer to this question indirectly by fluorescent studies, and work is being carried on with this in mind.

Conclusions

Only cations which form complexes with salicylates¹⁰ have any effect on the fluorescence. The results parallel those of STEVENS¹¹ who found that ions of the transition elements did not cause fluorescence in 8-quinolinol complexes. The effect of a very small ion which forms strong oxygen bonds is shown in the case of Be(II), which

produced both an increase in fluorescence intensity and also a change in the peak wavelength of the emission spectrum.

This investigation was supported by research grant No. 8005, from the National Institutes of Health, U. S. Public Health Service.

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- ¹ S. UDENFRIED, *Fluorescence Assay in Biology and Medicine*, Academic Press, New York, 1962.
- ² G. A. THOMMES AND E. LEININGER, *Anal. Chem.*, 30 (1958) 1361.
- ³ H. GOTO, *C. A.*, 36 (1941) 1720.
- ⁴ C. A. ZITTLE, L. PEPPER AND E. W. BINGHAM, *Arch. Biochem. Biophys.*, 88 (1960) 94.
- ⁵ A. ROSEN AND R. T. WILLIAMS, *Photoelec. Spectrometry Group Bull.*, No. 13, March 1961.
- ⁶ J. A. BISHOP, *Anal. Chim. Acta*, 29 (1963) August issue.
- ⁷ J. SCHUBERT, in *Metal Binding in Medicine*, SEVEN AND JOHNSON (Eds.), J. B. Lippincott, Philadelphia, Pennsylvania.
- ⁸ C. HEITNER-IRGUN AND R. COHEN, *Bull. Soc. Chim. France*, (1960) 293.
- ⁹ J. SCHUBERT AND A. LINDENBAUM, *J. Biol. Chem.*, 208 (1954) 359.
- ¹⁰ J. PECCI AND W. C. FOYE, *J. Am. Pharm. Assoc., Sci. Ed.*, 49 (1960) 411.
- ¹¹ H. M. STEVENS, *Anal. Chim. Acta.*, 20 (1959) 389.

(Received February 22nd, 1963)

Anal. Chim. Acta, 29 (1963) 84-87

A sensitive method for end-point detection in constant current coulometry

Constant current coulometric titrations of acids and bases have been described earlier¹. For high precision analysis with such a method the exact determination of the endpoint is important. Potentiometric methods of indication are very often used and we have therefore examined the sensitive detection method described elsewhere², for acid-base coulometric titrations. In the straightforward potentiometric titration, the endpoint is located by recording in the close neighbourhood of the endpoint the derivative of successive potential changes resulting from successive additions of very small quantities of titrating reagents (*e.g.* 0.010 ml of 0.1 *N* sodium hydroxide solution).

During a coulometric titration the equivalent of such successive additions can be realized by passing a current of exactly known intensity during a short time interval, *e.g.* 50 or 100 mA during 1 sec, 100 mA for 1 sec being about equivalent to the above mentioned amount of base. A similar technique has been described for a coulometric determination of phenol³. These short impulses of constant current intensity are produced by using a preset-time timer in connection with the current generator. The coulometer is calibrated by measuring the potential drop across high precision resistances that are included in the electrolysis circuit. Two resistances (R_1 and R_2 , Fig. 1) are used to control the current during the electrolysis and are themselves

Anal. Chim. Acta, 29 (1963) 87-89

calibrated during the main calibration of the whole apparatus. They are of such dimensions that currents of 50 and 200 mA can be controlled. We intend to replace the simple adjustment circuit later on by a self-regulating electronic circuit, that would keep the current automatically constant to about 0.01%.

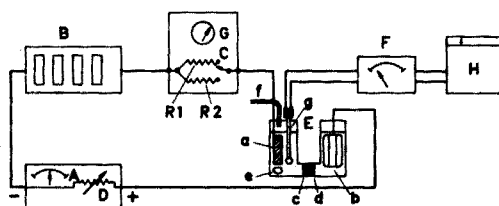


Fig. 1. Diagram of the coulometer.

- | | |
|---|--------------------------------------|
| A Constant current supplier | H Recorder (for end-point recording) |
| B Electronic timer | a Platinum cathode |
| C Potentiometer device for current adjustment control | b Silver anode |
| G Galvanometer | c Sintered glass |
| R ₁ , R ₂ Calibrated resistors | d Agar-agar plug |
| D Variable resistor for current adjustment | e Magnetic stirrer |
| E Cell | f Nitrogen entrance |
| F End-point indicator (pH meter) | g Glass-calomel electrode |

A diagram of the coulometer is shown in Fig. 1. The titration cell for acid-base titration has two cell compartments connected by a tube closed with a sintered glass disc and an agar-agar plug. The reduction of one equivalent of hydrogen occurs at the platinum gauze cathode and at the silver anode one equivalent of silver chloride is deposited. Before the beginning of a titration the current is adjusted by means of the resistance D to about 200 mA. Then the titration is started and the actual current is readjusted every 5 min so that the galvanometer G is always at zero. When the needle of the pH meter (F) begins to move rapidly, that is near the end-point, the current is switched off. Then successive impulses of 1 sec \times 100 mA are produced, and the nearer the end-point is approached, the higher becomes the resulting trace of the recorder. This is continued until the end-point has been passed by two or three impulses. In case of the boric acid titration after mannitol addition, the first and second end-points are recorded by just the same method. The total quantity of electricity (m in coulombs) that passes between the first and the second end-points corresponds to the boric acid titrated. This means that if readings are as follows:

n_0, n_1 = number of impulses after the first, and before the second end-point,

t_1 = duration of one impulse (sec),

t_2 = duration of the passage of the main current (sec),

i_1 = intensity of the current during the impulses (mA),

i_2 = intensity of the main current (mA),

then $m = (n_0 + n_1) t_1 \cdot i_1 + t_2 \cdot i_2$

The use of separate pH meter electrodes in the same titration compartment seems to be quite unsuitable. To avoid undue induction effects in the pH electrodes owing to the electric field, a standard combined glass calomel electrode is preferable to separating the calomel electrode and the platinum electrode from the titration cell by two salt bridges as in a method described earlier⁴. The exact positioning of this electrode is very important.

The method was tested for 0.1 *N* hydrochloric acid and a reproducibility of about 0.02% (relative standard deviation for a series of test results) was obtained. When this coulometric procedure was applied to the boric acid titration described previously², a reproducibility of the order of 0.065% was obtained. A comparison of the factors for the boron content obtained for the same solution of boric acid by chemical standardization and by coulometry gave the following results:

	<i>Factor</i>	<i>Relative standard deviation of the mean (95% probability level)</i>
Coulometric	30.8785	0.065%
Titrimetric	30.8562	0.04 %

The coulometric method is much faster and easier to apply than the previously described volumetric method.

In a later article complete details of the reproducibility, the accuracy and the instrumentation used will be described.

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¹ J. K. TAYLOR AND S. W. SMITH, *J. Res. Nat. Bur. Std.* 63A, 2 (1959) 153.

² K. F. LAUER AND Y. LE DUIGOU, *Z. Anal. Chem.*, 184 (1961) 4.

³ G. S. KOZAK AND Q. FERNANDO, *Anal. Chim. Acta*, 26 (1962) 541.

⁴ A. PARKER AND E. A. TERRY, *AERE Report AM-72*, 1961.

(Received February 25th, 1963)

Anal. Chim. Acta, 29 (1963) 87-89

A new microscopic crystal test for beryllium with hexamminocobalt(III) chloride

In the systematic qualitative analysis of the common elements extended to cover the elements W, Mo, Be, U, V, Ti and Zr, following the classical H₂S-system, beryllium and uranium can be isolated together by extraction of the precipitate of the ammonia group (Al, Fe, Cr, Be, U, Ti, Zr, V, (Mn)) with a 5% ammonium carbonate solution at a temperature of 65° (ref. 1). It is advisable to perform the extraction at 65° to prevent dissolution of more than traces of titanium and zirconium. The separation of beryllium from uranium can be accomplished in the carbonate extract by selective hydrolysis, whereupon beryllium and uranium can be detected microscopically by the BEHRENS² tests as potassium beryllium oxalate and thallos uranyl carbonate.

Anal. Chim. Acta, 29 (1963) 89-92

In practice, there are two objections to the application of the potassium beryllium oxalate test. The first objection is the great difference between the possible forms of the crystals, which depend on the beryllium concentration and the acidity. The second objection is that beryllium should be separated from uranium before the identification, because a precipitate of uranyl oxalate may be formed and may resemble the precipitate of potassium beryllium oxalate.

The precipitate formed by hexamminocobalt(III) chloride with the carbonate complex of beryllium in an ammonium carbonate solution can be utilized in a



Fig. 1. The precipitate formed by hexamminocobalt(III) chloride with an ammonium carbonate solution of beryllium (1 : 4000). $M = 100\times$.

microscopic identification of beryllium without the above-mentioned disadvantages. Our attention was drawn to this reaction by the work of PIRTEA AND MIHAIL³ who used the reaction product of hexamminocobalt(III) chloride and the carbonate complex of beryllium for a gravimetric determination of beryllium. The composition of the final precipitate was stated to be $\text{Co}(\text{NH}_3)_6 [(\text{H}_2\text{O})_2 \text{Be}_2(\text{OH})_3 (\text{CO}_3)_2] \cdot 3 \text{H}_2\text{O}$. An examination of this precipitate showed prismatic and rhombohedral crystals, but no mention was made of a microscopic test for beryllium.

The present study of hexamminocobalt(III) chloride as a reagent for the microscopic identification of beryllium has shown the attractive properties of this reagent: it offers a sensitive test on beryllium. A separation from uranium is superfluous and the test is specific in conjunction with the systematic qualitative analysis. Moreover, beryllium can be used immediately in the ammonium carbonate extract. The fresh precipitate of hexamminocobalt(III) chloride with the carbonate complex of

beryllium in an ammonium carbonate solution consists of regular triangles without birefringence and skeletons with birefringence.

The test is best performed as follows.

Place a droplet of the beryllium solution on the edge of a slide. If the solution already contains ammonium carbonate, as is the case when beryllium has been isolated by extraction of the precipitate of the ammonia group with a 5% ammonium carbonate solution, place a small drop of a 3% $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ solution in the immediate neighbourhood and move this drop into the first drop with a platinum wire: pale



Fig. 2. The precipitate formed by hexamminocobalt(III) chloride with an ammonium carbonate solution of uranium (1 : 200). $M = 100\times$.

yellow-brown regular triangles and skeletons indicate a positive test for beryllium (Fig. 1).

If the beryllium solution is acidic, add sufficient solid ammonium carbonate to make the solution alkaline; ensure that any white precipitate dissolves in the excess of ammonium carbonate. Then proceed as above. Limit of identification: $0.1\ \mu\text{g}$. Limit of dilution: 1 : 100,000

Uranium as the carbonate complex in a 5% ammonium carbonate solution can give a precipitate with hexamminocobalt(III) chloride; the needles formed can easily be distinguished from the precipitate of beryllium (Fig. 2). If the test is carried out as described above, the limit of identification for uranium is $2.5\ \mu\text{g}$ and the limit of dilution is 1 : 4000.

The limit of identification of beryllium is not affected by the presence of 200-fold amounts of uranium. As one can see from Fig. 3, the recognition of beryllium at a

dilution of 1 : 40,000 offers no difficulties in the presence of uranium at a dilution of 1 : 200. If beryllium is present at a dilution of 1 : 8000 and uranium at a dilution of 1 : 400, the crystals of the uranium precipitate do not develop or develop with difficulty, because the precipitate of beryllium is much less soluble and consumes the reagent first. Thus, much uranium does not interfere inconveniently with the identi-

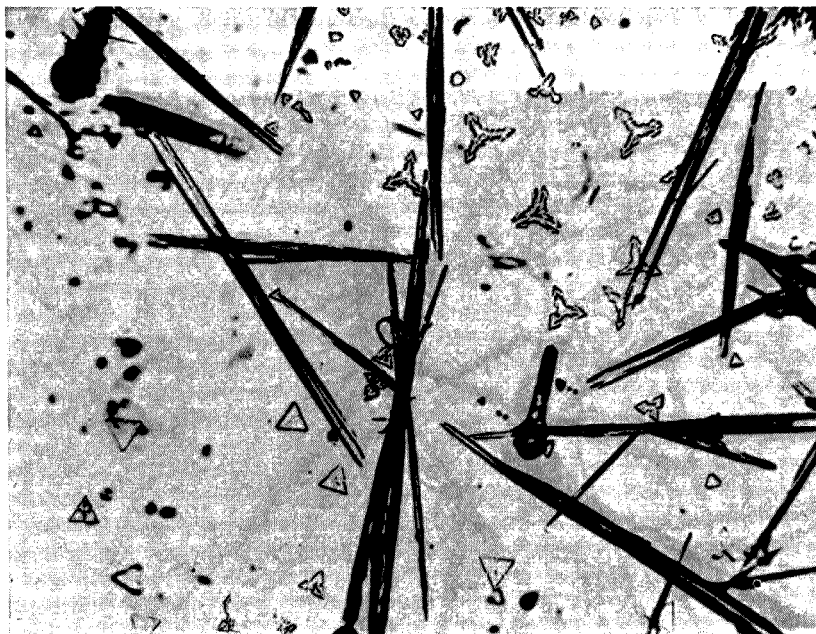


Fig. 3. The precipitate formed by hexamminocobalt(III) chloride with a 5% ammonium carbonate solution of beryllium (1 : 40,000) (triangles, three-pointed stars) + uranium (1 : 200) (needles).
M = 100 \times .

fication of beryllium; whereas a little beryllium interferes with the identification of uranium if hexamminocobalt(III) chloride is employed.

The carbonate complexes of titanium, zirconium, indium and gallium, prepared by extraction of the hydroxides with a 5% ammonium carbonate solution at room temperature give no reaction with hexamminocobalt(III) chloride.

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¹ C. J. VAN NIEUWENBURG AND J. W. L. VAN LIGTEN, *Qualitative Chemische Analyse*, Springer-Verlag, Wien, 1959, p. 215.

² H. BEHRENS, *Anleitung zur mikrochemischen Analyse*, Verlag Voss, Hamburg, 1899.

³ TH. I. PIRTEA AND G. MIHAIL, *Z. Anal. Chem.*, 159 (1957/58) 206.

(Received March 24th, 1963)

Book Reviews

I.A. VOINOVITCH, J. DEBRAS-GUÉDON ET J. LOUVRIER, *L'Analyse des Silicates*. Editions scientifiques Hermann, Paris, 1962, 512 pp., 48 F.

L'analyse des silicates est restée pendant de nombreuses années un exemple-type d'analyse quantitative classique par séparations par précipitation et dosages gravimétriques. En effet le dosage de la silice, de l'alumine, des alcalino-terreux et des alcalins ont été les derniers à subir des modifications. Le développement des méthodes colorimétriques et complexométriques, de la spectrophotométrie de la flamme, les progrès de la spectrophotométrie d'émission en ce qui concerne les poudres, l'apparition de la fluorescence-X comme méthode de dosage, ont apporté des modifications nombreuses dans ce domaine.

Le présent ouvrage est le premier de cette ampleur qui fait le point de cette question. Il est de plus écrit par des spécialistes qualifiés possédant une très longue expérience personnelle au Centre National d'Etudes et de Recherches Céramiques et une grande expérience des méthodes utilisées dans le monde entier.

Dans la 1^{ère} partie de l'ouvrage sont décrits les principes généraux des méthodes physiques mises en oeuvre (144 pages). Dans une seconde partie sont abordées les techniques analytiques générales: méthodes chimiques (100 pages), spectroscopie optique d'émission (60 pages). Les modes opératoires sont ensuite décrits élément par élément pour 27 d'entre eux.

Des méthodes nouvelles sont données.

Des techniques d'analyse de silicates complexes tels que: émaux, céramiques, chromites, laitiers, zircons, certains minerais de fer, etc. sont également exposées dans ce vaste ouvrage. Les techniciens qui ont à analyser des silicates trouveront des modes opératoires détaillés qu'ils pourront utiliser directement, sans avoir à en faire une mise au point ou une adaptation préalable.

En outre, les méthodes et les modes de dosage décrits intéressent tous les laboratoires d'analyse.

L'ouvrage est parfaitement présenté.

G. CHARLOT (Paris)

Anal. Chim. Acta, 29 (1963) 93

Electrolytes: Proceedings of an International Symposium held in Trieste, June 1959. Edited by B. PASCE. Pergamon Press, Oxford, 1962. Pp vii + 360. Price £ 5.0.0.

This volume contains thirty-two papers which were presented at a symposium which formed part of the 47th Reunion of the Societa Italiana per il Progresso delle Scienze. Six of the papers are in Italian, three in German, one in French, and the remainder in English. The main themes are ion-ion interactions and ion-solvent interactions in electrolyte solutions, both aqueous and non-aqueous. Some of the most interesting articles are concerned with the detailed interpretation of the conductance of electro-

Anal. Chim. Acta, 29 (1963) 93-94

lyte solutions, and much use is made of the Fuoss-Onsager conductance equation. It is gratifying to see attention being directed not only to the concentration dependence of conductance, but also increasingly to the absolute values of ionic conductance at infinite dilution in relation to ion size and interaction with the solvent. There are also several papers on the equilibrium properties of electrolyte solutions, and here again the role of ion-solvent interactions is considered as well as that of interionic forces. Some of the papers are purely theoretical and concerned mainly with electrolyte solutions from the point of view of statistical mechanics, but the majority either present new experimental data or survey existing data, and discuss its theoretical interpretation. Altogether the articles in this volume provide a good indication of current trends and interests in the study of electrolyte solutions.

J. E. B. RANGLES (Birmingham)

Anal. Chim. Acta, 29 (1963) 93-94

Comprehensive Analytical Chemistry, Volume IC., Classical Analysis, Editors C. L. and D. W. WILSON. Elsevier Publishing Company, Amsterdam, 1962. Pp. xxx + 728. Price. Dfl. 70,00.

This third part of Volume I of *Comprehensive Analytical Chemistry* completes the discussions of classical analysis in this encyclopedia, and contains a systematic treatment of the analysis of the elements. Thirty analytical chemists have contributed to the present text; this has made it difficult to obtain a uniform style and treatment for each element, although it has the advantage that the most suitable authors have been commissioned to write about particular elements. In most cases, a reasonably comprehensive account of the various gravimetric and titrimetric procedures available for individual elements is given, with full references and details of the methods which are regarded as the most satisfactory. Indeed, it would be invidious in a compilation of this sort to criticise individual articles for literary style. However, criticism of chemical content is justified and in this respect, model articles have been provided on the alkali metals, aluminium, fluorine and the platinum metals.

On the whole, the present text has few serious shortcomings. Certain omissions are perhaps inevitable in a compilation prepared by so many contributors. However, these are of minor significance when the value of the completed Volume I is considered. It is obvious that this will remain a standard work of reference for many years to come.

W. I. STEPHEN (Birmingham)

Anal. Chim. Acta, 29 (1963) 94

Theory and Applications of Ultraviolet Spectroscopy, H. H. JAFFÉ AND M. ORCHIN, J. Wiley and Sons, New York, 1962, pp. xv + 624. 113 s.

The rapid expansion in the use of instrumental methods for analytical and structural purposes had, until recently, not been accompanied by any corresponding increase in the number of suitable text-books. This has been particularly true of spectroscopic

Anal. Chim. Acta, 29 (1963) 94-95

methods and in this context this authoritative book by Professors Jaffé and Orchin is to be especially welcomed.

The book presents first the necessary theoretical discussion of electronic states and light absorption and then applies these concepts to the interpretation of the electronic spectra of organic compounds. The authors have sensibly omitted all but the briefest mention of instrumentation and of experimental methods and procedures.

The theoretical section starts with a lucid account of elementary molecular orbital theory and symmetry operations. From this basis subsequent chapters discuss selection rules and intensities, and the nature of the excitation process and excited states in a manner comprehensible to all but the least mathematical chemist; a mathematically more detailed account is usefully presented concurrently using sections in small print. The analysis of empirical spectral properties follows the logical sequence of increasing complexity: simple chromophores, conjugated systems, aromatic molecules, and steric effects. The wealth of experimental data has precluded any attempt to make these chapters comprehensive and the selection which has been exercised clearly reflects the authors' own interests. The consequently uneven treatment of these chapters, while not affecting its use as a text-book, reduces the value of the book for reference purposes. In the last five chapters attention is given to a number of currently important topics: the spectra of free radicals, of sulphur and phosphorus compounds, of inorganic complexes, fluorescence and phosphorescence, and some applications to quantitative analysis.

In both design and presentation this book admirably fulfills the aims of its authors to present a firm foundation for understanding and using absorption spectroscopy; it deserves wide success.

K. J. MORGAN (Birmingham)

Anal. Chim. Acta, 29 (1963) 94-95

Announcement

MODERN METHODS IN THE ANALYSIS OF ORGANIC COMPOUNDS

A Symposium on modern methods in the analysis of organic compounds will be held on May 20-23rd, 1964, in Eindhoven (Holland), organized by the Analytical Chemistry Divisions of the Gesellschaft Deutscher Chemiker and of the Koninklijke Nederlandse Chemische Vereniging, and with the patronage of the Analytical Chemistry Section of IUPAC.

Topics for the Symposium are planned as follows:

1. Elemental analysis; functional group analysis.
2. Constitution of organic compounds; molecular spectroscopy.
3. Separation processes; diffusion and chromatographic methods.
4. Analysis of high polymers.
5. Analysis of natural substances; clinical analysis.

Anal. Chim. Acta, 29 (1963) 95-96

The programme will become available at the beginning of 1964. Further information can be obtained from GDCh-Geschäftsstelle, 6000 Frankfurt (Main), Postfach 9075, Federal Republic of Germany.

Anal. Chim. Acta, 29 (1963) 95-96

Publications Received

Allgemeine Chemie, HANS RUDOLF CHRISTEN, Otto Salle Verlag, Frankfurt am Main - Hamburg, 1963, pp. 200 (no price given).

Atom Bindung Reaktion: Anschauliche Einführung in die theoretischen Grundlagen, ANTON STIEGER, Otto Salle Verlag, Frankfurt am Main - Hamburg, 1963, pp. 123 (no price given).

L'Eau, CLÉMENT DUVAL ("Que sais-je?" Le Point des Connaissances Actuelles No. 266), Presses Universitaires de France, Paris, 1962, pp. 126 (no price given).

L'Air, CLÉMENT DUVAL ("Que sais-je?" Le Point des Connaissances Actuelles No. 1034), Presses Universitaires de France, Paris, 1963, pp. 128 (no price given).

The Case against the Nuclear Atom, DEWEY B. LARSON, North Pacific Publishers, Portland (Oregon), 1963, pp. 139. Price \$ 4.50 (post paid).

Química Analítica Cuantitativa, F. BERMEJO MARTINEZ, 2.a edición, Imprenta del Seminario Conciliar, Santiago de Compostela, 1963, pp. xv + 1258 (no price given).

The Detection and Determination of Antioxidants in Food (Special Report No. 1, 1963). The Association of Public Analysts, London S.E.1, 1963, pp. 27. Price 10 s. (post paid).

Determination of Trace Elements, with Special Reference to Fertilisers and Feeding Stuffs, prepared by the Analytical Methods Committee of the Society for Analytical Chemistry, W. Heffer and Sons Ltd., Cambridge, 1963, pp. vii + 39. Price 21 s.

Anal. Chim. Acta, 29 (1963) 96



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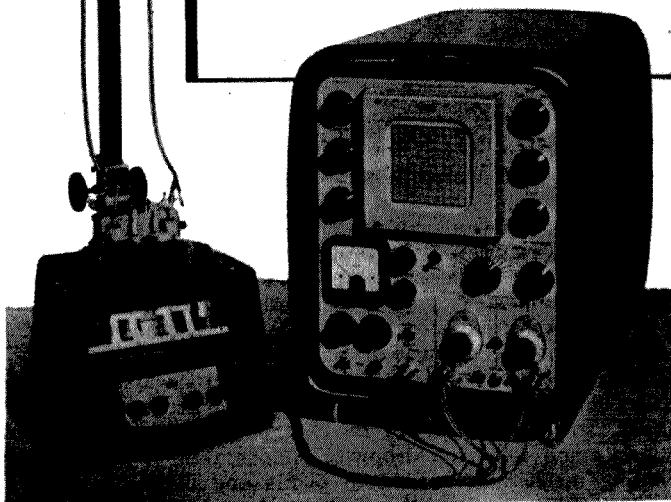
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The work is designed as an introduction to students and as a guide to advanced work in the field of textile chemistry.

contents

1. Introduction. 2. Condensation polymers. 3. Addition polymers. 4. Co-polymers. 5. Molecular weight determination. 6. Cotton and flax. 7. Chemistry of cellulose. 8. Amino acids and proteins. 9. Synthetic polypeptides. 10. Wool. 11. Silk. 12. Crystalline structures of polymers. 13. Melting and crystallization. 14. Fine structure. 15. Production of fibres. References. Index.

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(1) Sen, B. N., *Anal. Chim. Acta*, 1961, 24, 386-7.

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(1) British Patent No. 806,935.

(2) Schurz, J. and Stubchen, H., *Z. Elektrochem.*, 1957, 61, 754-63.

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(1) Marquet, A., *et al.*, *Bull. Soc. chim. France*, 1961, 1822-31.

(2) Marquet, A. and Jacques, J., *Bull. Soc. chim. France*, 1962, 90-96.



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CONTENTS

Méthode continue pour le dosage de l'acide carbonique en faibles concentrations J. P. EHRENBURG ET G. B. SMIT (Arnhem, Netherlands)	1
Gravimetric determination of cobalt as presumed $K_2Co(NO_2)_6$ J. J. LINGANE, P. J. LINGANE AND M. D. MORRIS (Cambridge, Mass., USA)	10
Determination of traces of free acid in uranyl salt solutions J. MASHALL AND A. BAR-NUN (Tel-Aviv, Israel)	22
Spectrophotometric determination of molybdenum with 8-mercaptoquinoline R. J. MAGEE AND A. S. WITWIT (Belfast, Great Britain)	27
Studies on uronic acid materials. Part VIII. A comparative study of some colorimetric methods of estimating the uronic acid contents of polysaccharides D. M. W. ANDERSON AND S. GARBUTT (Edinburgh, Great Britain)	31
Part IX. The simultaneous determination of uronic acid and alkoxy groups in polysaccharides by reflux with hydriodic acid D. M. W. ANDERSON, S. GARBUTT AND S. S. H. ZAIDI (Edinburgh, Great Britain)	39
Kinetics of the extraction of chromium(III) into chloroform containing acetylacetone H. E. HELLWEGE AND G. K. SCHWEITZER (Knoxville, Tenn., USA)	46
The determination of titanium in meteoritic material A. J. EASTON AND L. GREENLAND (Canberra, Australia)	52
Studies on the solvent extraction of yttrium thenoyltrifluoroacetate G. K. SCHWEITZER AND S. W. McCARTY (Knoxville, Tenn., U.S.A.)	56
Polarographic determination of indium in lead and zinc metals R. J. HOFER, R. Z. BACHMAN AND C. C. BANKS (Ames, Iowa, USA)	61
<i>Short communications</i>	
Étude thermogravimétrique des picolates et dipicolates de lanthane, praséodyme et néodyme L. MOYNE ET G. THOMAS (Lyon, France)	66
A modified method for the titrimetric determination of manganese in ores and metals J. DOLEŽAL, J. ZÝKA AND G. DONOSE (Prague, Czechoslovakia and Santiago, Chile)	70
Analytical possibilities of a series of new aromatic-type chelate compounds A. J. CAMERON, N. A. GIBSON AND R. ROPER (Sydney, Australia)	73
Determination of some organic halides by formation of Bunte salts with thiosulphate and iodimetry M. R. F. ASHWORTH AND M. WINTER	75
Infrared spectrophotometry of aqueous nitrate, nitrite and sulfate solutions A. L. UNDERWOOD, M. W. MILLER AND L. H. HOWE (Atlanta, USA)	81
Determination of traces of copper L. DE ROO, J. F. M. TERTOOLEN AND C. BUIJZE (Delft and Rijswijk, Netherlands)	82
Titrimetric determination of iron(III) with titanium(III) at room temperature. Safranin T, phenosafranin and neutral red as indicators P. V. KRISHNA RAO AND G. GOPALA RAO (Waltair, India)	84
Complex formation and fluorescence. Part III. Salicylate complexes J. A. BISHOP (Newark, USA)	85
A sensitive method for end-point detection in constant current coulometry K. F. LAUER AND Y. LE DUIGOU (Geel, Belgium)	87
A new microscopic crystal test for beryllium with hexamminocobalt(III) chloride J. W. L. VAN LIGTEN AND W. COOL (Delft, Netherlands)	89
Book reviews	93
Announcement	95
Publications received	96

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