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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 26, No. 3, March 1962

A STUDY OF THE THEORETICAL EFFECT OF A COMPLEXING AGENT IN COUNTERCURRENT EXTRACTION

A general relationship between the variables involved in the countercurrent extraction of a solute by the formation of a 1 : 1 complex in the extracting solution has been found. Equations were fitted to the results obtained when an electronic computer was used to calculate the equilibria at each stage of the extraction transfer processes. Combination of these has yielded a final expression of simple form.

B. C. Cox, *Anal. Chim. Acta*, 26 (1962) 197–203

LIQUID–LIQUID EXTRACTION OF ZIRCONIUM WITH TRI-*n*-OCTYLAMINE AND DIRECT COLORIMETRIC DETERMINATION WITH XYLENOL ORANGE

A new, very sensitive method for the non-aqueous colorimetry of zirconium is described. Tri-*n*-octylamine solutions obtained by liquid–liquid extraction of Zr from the initial 11 *N* HCl solution are used with xylenol orange as reagent. For pyridine buffered systems a 1 : 1 complex is formed with insufficient reagent and a 1 : 2 complex with excess of reagent. For systems buffered with acetic acid, only the 1 : 1 complex is formed (absorption maximum 550 mμ; $\varepsilon = 53{,}300$).

The acetic acid method is more sensitive and many foreign ions can be tolerated. Zirconium can be determined in the presence of 10,000 times its amount of non-extractable ions (such as alkali metals, alkaline earths, rare earths, aluminium, etc.) and of 100 or 10 times its amount of many other elements which are extracted by the amine.

E. Cerrai and C. Testa, *Anal. Chim. Acta*, 26 (1962) 204–211

THE DETERMINATION OF TRACE AMOUNTS OF TOTAL NITROGEN IN PETROLEUM DISTILLATES EXTRACTIVE PERCOLATION METHOD

A new method is presented for the determination of trace amounts of total nitrogen in petroleum distillates ranging from gasolines to lubricating oils. The method is based on percolation of the sample through concentrated sulphuric acid distributed on a carrier. Owing to its high precision the proposed method allows a sharp differentiation between nitrogen contents even at levels below 10 p.p.m. Factors which commonly interfere with the detection of traces of nitrogen are minimized. The relative simplicity of the method makes it suitable for routine application.

P. Gouverneur, *Anal. Chim. Acta*, 26 (1962) 212–223

SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE IN HUMAN PLASMA AND RED CELLS WITH BENZOHYDROXAMIC ACID

A spectrophotometric method for the determination of manganese in human plasma and red cells with benzohydroxamic acid is presented. Interfering ions are removed by an anion exchange method, using Dowex-1, 8X resin. The manganese concentration found for plasma and red cells was about 0.1 and 0.2 p.p.m., respectively.

D. O. MILLER AND J. H. YOE, *Anal. Chim. Acta*, 26 (1962) 224–229

SPECTROPHOTOMETRIC DETERMINATION OF ALIPHATIC ALDEHYDE 2,4-DINITROPHENYLHYDRAZONES WITH 3-METHYL-2-BENZOTHIAZOLINONE HYDRAZONE

A sensitive new spectrophotometric procedure is described for the analysis of aliphatic aldehyde 2,4-dinitrophenylhydrazones. The chromogens formed in the procedure absorb at 667 mμ and are approximately three times as intense at this band as the starting aldehyde derivatives are in neutral and alkaline solvent at their wavelength maxima. With further improvement the procedure is capable of even greater sensitivity. Other aliphatic aldehyde derivatives also should be analyzable by this procedure, but 2,4-dinitrophenylhydrazones of ketones do not react.

E. SAWICKI, TH. R. HAUSER AND F. T. FOX, *Anal. Chim. Acta*, 26 (1962) 229–234

SPECTROPHOTOMETRIC DETERMINATION OF URANIUM(VI) BY THE AZIDE REACTION

Azide has been investigated as a spectrophotometric reagent for uranium(VI). The system is more sensitive than the thiocyanate reaction. It obeys Beer's law in the range 2–180 p.p.m. of uranium. The colour is sensitive to hydrogen ion concentration; maximum absorbance and stability are attained at pH 5–5.5. Iron(III) interferes seriously, but can be masked by EDTA. Fe^{+2}, Cr^{+3}, Ni^{+2}, Th^{+4}, $Cr_2O_7^{-2}$, WO_4^{-2}, VO_3^- and F^- interfere. The deep yellow colour cannot be extracted with organic solvents. A mono-azido-uranium(VI) ion is present in dilute solutions; its dissociation constant is $2.3 \pm 0.27 \cdot 10^{-3}$.

F. G. SHERIF AND A. M. AWAD, *Anal. Chim. Acta*, 26 (1962) 235–241

PHOTOMETRIC DETERMINATION OF ZINC IN METEORITES

Zinc is determined in iron and silicate meteorites by the spectrophotometric dithizone method after separation from iron(III), nickel, cobalt, copper and other elements by ion exchange on Dowex 1-X8 resin in hydrochloric acid solution. The distribution of zinc is so heterogeneous in some irons and chondrites that 1-g samples do not give reproducible values.

M. NISHIMURA AND E. B. SANDELL, *Anal. Chim. Acta*, 26 (1962) 242–248

COLORIMETRIC MICRODETERMINATION OF CYSTINE AND CYSTEINE

Thiofluorescein is bleached in alkaline medium by light but reforms its colour on reaction with —SH groups. This can be used for the colorimetric determination of cystine and cysteine in the micromolar range.

P. DUBOULOZ, J. FONDARAI AND R. PAVONE-MARVILLE, *Anal. Chim. Acta*, 26 (1962) 249–252

THE DETERMINATION OF SOME ALIPHATIC ALCOHOLS AND ALDEHYDES BY OXIDATION WITH ACID POTASSIUM DICHROMATE

The oxidation of *n*-propanol and *n*-butanol and the corresponding aldehydes by dilute acid potassium dichromate has been investigated. Some carbon–carbon bond fission occurs, and it has been shown that this takes place via the enol form of the aldehyde formed in the first stage of the oxidation. However, the proportion of this degradation is constant over a wide range of conditions and the method is capable of being used for the quantitative determination of simple aliphatic alcohols and aldehydes.

J. A. BARNARD AND N. KARAYANNIS, *Anal. Chim. Acta*, 26 (1962) 253–258

THE MINIMUM BUFFER CAPACITY IN POTENTIOMETRIC TITRATIONS

(in German)

For all symmetrical titrations the minimum of the buffer capacity, *i.e.* the differential quotient dv/dE, coincides with the equivalence point. For asymmetrical titrations the differences between the minimum and the equivalence volumes have been calculated; the numerical values are given.

F. L. HAHN, *Anal. Chim. Acta*, 26 (1962) 258–264

QUANTITATIVE CHROMATOGRAPHIC ANALYSIS USING RECTIFIED RADIO FREQUENCY METHODS

PART II. FLUORIDE, CHLORIDE, BROMIDE AND IODIDE

A new developing solvent is described for the paper chromatographic separation of sodium fluoride, chloride, bromide, and iodide. The separated ion zones are located by the BLAKE Zone Detector, and the amount of halide ions present determined by measurement of the impedance of their respective aqueous extracts.

J. A. BROOMHEAD AND N. A. GIBSON, *Anal. Chim. Acta*, 26 (1962) 265–268

DETERMINATION OF RHODIUM BY THERMAL NEUTRON ACTIVATION ANALYSIS USING γ-RAY SPECTROMETRY

Trace amounts of rhodium have been determined by thermal neutron activation analysis using both destructive and non-destructive methods. With a neutron flux of 10^{12} n cm^{-2} sec^{-1} the lower limits of detection are about 0.1 μg and 0.01 μg, respectively. A rapid sodium peroxide fusion followed by a pyridine extraction was used in the destructive method to separate the 4.4-min ^{104m}Rh from its matrix. The 44-sec ^{104}Rh was used in the non-destructive method. Both radioactive isomers were measured by γ-ray spectrometry with a multichannel pulse height analyzer. The average time required per non-destructive analysis was 7 min while the chemical method averaged 20 min.

E. L. STEELE AND W. W. MEINKE, *Anal. Chim. Acta*, 26 (1962) 269–274

DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC FLUORINE COMPOUNDS

A rapid determination of carbon and hydrogen in organic fluorine compounds is described. Magnesium oxide is used both as an absorbent for fluorine and as an aid to complete combustion. The time required for one determination in series is under 30 min. The method is very widely applicable.

A. D. CAMPBELL AND A. M. G. MACDONALD, *Anal. Chim. Acta*, 26 (1962) 275–280

DETERMINATION OF SOLUBLE AND INSOLUBLE ZIRCONIUM IN MAGNESIUM ALLOYS

A method for the determination of soluble and insoluble zirconium is described. To differentiate between the two forms, two solutions are prepared, in one of which the insoluble zirconium remains in suspension; in the other it is brought into solution with hydrofluoric acid. Zirconium is extracted by trioctyl phosphine oxide/petroleum ether and determined in the extract spectrophotometrically with pyridyl-azo-naphthol (PAN) as reagent.

R. H. A. CRAWLEY, *Anal. Chim. Acta*, 26 (1962) 281–284

CHLORPROMAZINE HYDROCHLORIDE AS AN ANALYTICAL REAGENT

PART I. SPOT TESTS FOR INORGANIC IONS

Chlorpromazine hydrochloride is proposed as a spot test reagent for the detection of gold, cerium, iron, chromate, manganate, bromate, iodate, nitrite, bromide, iodide, platinum and palladium. Conditions for the suppression of certain interfering substances are also given.

LEE KUM-TATT, *Anal. Chim. Acta*, 26 (1962) 285–289

MASKING ACTION OF COMPLEXANS ON QUALITATIVE INORGANIC REACTIONS

The masking action exerted by 20 complexans on the course of many tests used in the qualitative inorganic analyses of cations is examined and recorded.

W. HOYLE, I. P. SANDERSON AND T. S. WEST, *Anal. Chim. Acta*, 26 (1962) 290–300

A STUDY OF THE THEORETICAL EFFECT OF A COMPLEXING AGENT IN COUNTERCURRENT EXTRACTION

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(Received June 26th, 1961)

INTRODUCTION

In some studies of the countercurrent extraction of halogen and interhalogen compounds from carbon tetrachloride solution with aqueous alkali halide solutions, it was found desirable to be able to relate the location of a particular polyhalide ion after N-extractions, to the dissociation constant of the ion.

A search of the literature of countercurrent extraction did not reveal any analysis of similar problems the results of which could be applied to this case, since the theories for linear partition isotherms[1] do not permit modification to allow for non-linearity.

FREY AND SCHEIBEL[2] have described a method for determining the number of stages required to achieve a required extraction when the partition isotherm is non-linear, which could be modified to suit the present problem. The calculations involved, however, would be excessively tedious and time-consuming, and it was decided that the method described in the present paper would give more satisfactory results.

The quantities which may vary from one extraction to another and which control the concentration changes during the extractions are: D, the partition coefficient of the halogen between carbon tetrachloride and water; c, the initial concentration of halogen in the carbon tetrachloride layer of the first extraction tube; A, the activity of the halide ions in the extracting solution; K, the instability constant of the polyhalide ion formed during the extractions; V_1 and V_2, the volumes of the carbon tetrachloride and aqueous phases in each extraction tube and N, the number of extraction cycles performed.

If X_2 represents the halogen being extracted from the carbon tetrachloride layer by distribution between the two phases and by the formation of polyhalide ion X_2Y^- with the halide ion Y^- in the aqueous phase, the relations which govern the equilibrium in any extraction tube are:

$$D = a_{X_2}\,(\text{in } CCl_4)/a_{X_2}\,(\text{in } H_2O) \qquad \text{(a)}$$

and

$$K = (a_{X_2} \cdot a_{Y^-})/a_{X_2Y^-} \qquad \text{(b)}$$

for the dissociative equilibrium of the polyhalide ion, according to $X_2Y^- \rightleftharpoons X_2 + Y^-$.

Considerable simplification of the calculation of the equilibrium can be achieved by (*i*) using an apparatus for which $V_1 = V_2$, so that the amounts of halogen present in each phase either as free halogen or polyhalide ion may be adequately represented

by the relevant activities, and (*ii*) utilising the facts that the formation of polyhalide ion does not alter the ionic strength of the aqueous solution; and that the activity coefficient of a non-electrolyte in electrolyte and non-electrolyte solutions can be shown for dilute solutions to be very close to unity. When these simplifications are inserted in eqns. (a) and (b) they become

$$D = [X_2]_{CCl_4}/[X_2]_{H_2O}$$

and

$$\begin{aligned} K &= (\gamma_{X_2} \cdot [X_2]\,\gamma \pm [Y^-])/\gamma'_{\pm}[X_2Y^-] \\ &= ([X_2][Y^-])/[X_2Y^-] \\ &= K_c \end{aligned}$$

if the reasonable assumption that $\gamma_{\pm} = \gamma'_{\pm}$ is made; from which

$$[X_2]_{H_2O} = (K \cdot [X_2Y^-])/(A - [X_2Y^-])$$

$$[X_2]_{CCl_4} = (D \cdot K[X_2Y^-])/(A - [X_2Y^-])$$

Halogen is also present in the aqueous phase as the polyhalide ion, and for the equilibrium in the first extraction tube after the first extraction, the balance

$$c = [X_2Y^-] + [X_2]_{H_2O} + [X_2]_{CCl_4}$$

may be set up, and used to find that

$$[X_2Y^-] = \tfrac{1}{2}[(c + A + DK + K) - \{(c + A + DK + K)^2 - 4cA\}^{\frac{1}{2}}]$$

from which $[X_2Y^-]$ and hence $[X_2]_{CCl_4}$ and $[X_2]_{H_2O}$ may be calculated if specific values of c, A, D and K are inserted. It can be seen, however, that a general expression for the distribution of halogen between the two phases in the n'th tube after N extractions and transfers, would be tedious to derive and not simple in form since a new value of c would have to be used for each pair of phases after each transfer and subsequent equilibration. Alternatively, the equilibrium in each extraction tube after each transfer could be calculated for several sets of D, K, A, c, data, and relationships between these variables found empirically. These calculations, whilst lengthy by ordinary methods, can be made quickly with an electronic computer. Because of their repetitive nature, once a suitable programme had been devised the calculations could be performed at night when the computer available in this college is normally unused.

EXPERIMENTAL

Preliminary studies

Initially, calculations were made with a simple test programme which gave the contents of all the extraction tubes after N extractions and transfers. In this way results such as those shown in Fig. 1 were obtained. Here the amount of halogen in the carbon tetrachloride layer of each extraction tube is graphed against the number of the extraction tube after $N = 20, 40, 60 \ldots$ extractions, for the values of D, K, A and c shown. When these points are joined by a smooth curve a hypothetical non-

integral tube number T_m at the maximum can be found. Fig. 2, a graph of N against T_m shows that T_m is directly proportional to N, and that the line makes a small positive intercept on the T_m-axis. This linearity has been shown by two trial calculations to

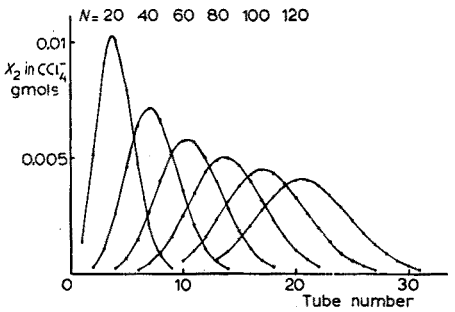

Fig. 1. Distribution of halogen amongst CCl_4 layers of extraction tubes after N transfers and equilibrations. $c = 0.025$; $D = 10$; $A = 0.05$; $K = 0.05$.

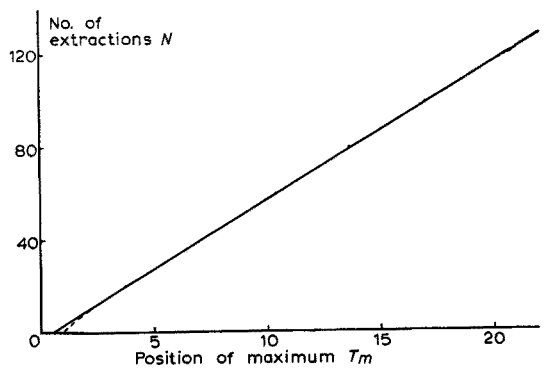

Fig. 2. Dependence of the value of the tube number, T_m, (hypothetical, non integral), at the maxima of the distribution curves shown in Fig. 1, on the number of extractions, N, performed.

continue to at least $N = 350$, whilst a more detailed graph indicates a slight curvature from $N = 0$ to $N = 20$, shown dashed in the figure, due to the gradual establishment of the smooth maxima exhibited when $N > 20$. These results indicated that after about 20 extractions T_m and N could be related by

$$T_m = S \cdot N + i \qquad (1)$$

Final programme

This was designed to measure the slope and intercept of the T_m/N relationship for any set of values of c, D, K and A, using the T_m-values given by a maximum finding subrouting after $2n$, $3n$, $4n$ ... extractions, where n can take any value, but was usually given the value of 10. The standard deviation of the slope of this line was also calculated and used to check the linearity of the graph. The calculations were programmed in simple code and carried out with a Stantec Zebra electronic computer.

Treatment of results

The intercepts i of the extrapolated linear part of the T_m against N graphs at $N = 0$ are small and very sensitive to errors in the estimation of the slope of the graphs. No significant variation of these intercepts with any of the variables c, D, K or A is apparent, and the mean value (for all the calculations performed) of $+0.38$ with a standard deviation of 0.02 is used in eqn. (5). On the other hand, the slopes S of these graphs vary as expected between $S = 1$ for $K = 0$, and a limiting value for $K = \infty$ when the extraction is controlled solely by the partition coefficient. This limiting value can be found from the formula[3] $T_m = (ND'r)/(D'r + 1)$ where r is the ratio V_1/V_2 and D' is the reciprocal of D used in these calculations, from which

$$S = \frac{dT_m}{dN} = \frac{1}{1 + D} \tag{2}$$

Provided that $c \leqslant A/2$ the value of S for a particular set of values of D, K and A is sensibly constant, as is illustrated in Table I.

TABLE I

D	K	A	c	S
1	0.5	0.5	0.05	0.667
1	0.5	0.5	0.1	0.669
1	0.5	0.5	0.25	0.666
10	0.1	0.5	0.05	0.373
10	0.1	0.5	0.1	0.372
10	0.1	0.5	0.25	0.373
10	0.1	0.5	0.5	0.367
10	0.05	0.25	0.05	0.372
10	0.05	0.25	0.1	0.374
10	0.05	0.25	0.25	0.367

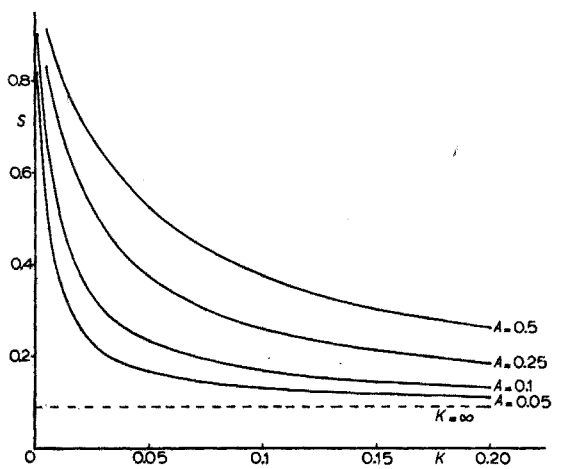

Fig. 3. Variation of the slopes S of Fig. 2 with activity A of the complexing agent and the instability constant K of the complex formed for a particular value of D. $D = 10$; $c \leqslant A/2$.

The main effect of the c/A ratio is on the distribution of the halogen amongst the extraction tubes about T_m.

The variation of S with K for $D = 10$ and for certain values of A is shown in Fig. 3, the limiting value of S for $K = \infty$ being shown dashed. These curves are adequately represented by the function

$$S/(1 - S) = M/K + I \tag{3}$$

for the values of S up to 0.8, as is shown by Fig. 4 in which it can be seen that when $S/(1 - S)$ is plotted against $1/K$ a linear relationship for each value of A is obtained, each line having the same intercept of 0.1 on the ordinate when $K = \infty$.

As S increases beyond 0.8 the $S/(1 - S)$ against $1/K$ relationship becomes increasingly non-linear, this effect being due to the asymmetry in the distribution of halogen concentration about T_m, which results in $S/(1 - S)$ against $1/K$ plots showing an inflection between $S = 0.8$ and $S = 1.0$; the larger the value of D the closer this inflection is to the ordinate axis.

For this reason graphs of $S/(1 - S)$ against $1/K$ have been constructed rather than of $(1 - S)/S$ against K, so that the graphs in Fig. 4 are constructed from data for which $0 < S < 0.8$ or $0 < S/(1 - S) < 4$.

The constant M in eqn. (3) may still contain terms involving D and A, and the

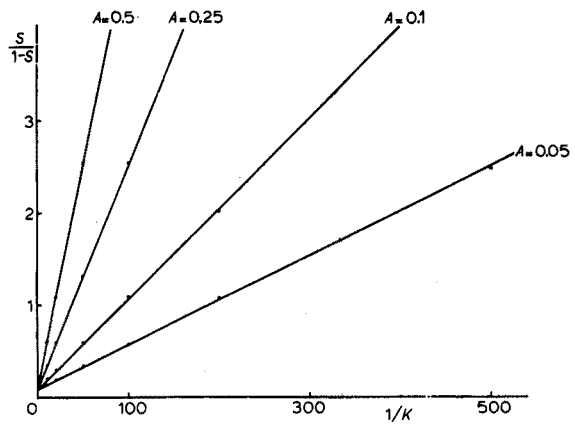

Fig. 4. Linearisation of the curves shown in Fig. 3 by the use of $S/(1 - S)$ against $1/K$ plots.

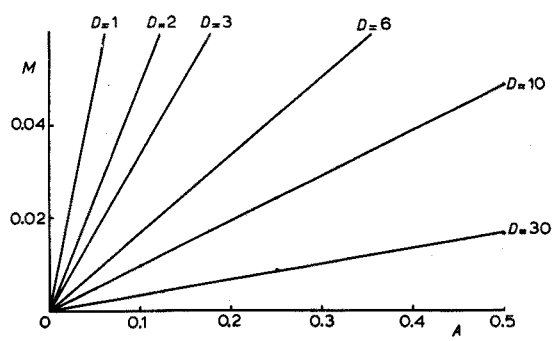

Fig. 5. The effect of A on the slopes of the lines in Fig. 4 for various values of the partition coefficient.

graph of M against A for $D = 10$ in Fig. 5 shows that $M = M'A$. A similar treatment of data for $D = 1$, 2, 3, 6, and 30 also gives linear relations of M and A. The data for $D = 30$ is included in this figure, and lines representative of the slopes obtained for $D = 1$, 2, 3 and 6 have also been inserted.

It is apparent at this stage, therefore, that

$$S/(1-S) = M'A/K + I \tag{4}$$

The value of the intercept I is given by the value of $S/(1-S)$ when $K = \infty$, which can be found from eqn. (2) to be $1/D$.

The constant M' is controlled by the distribution coefficient, and a graph of M' against $1/D$ has a slope of unity and passes through the origin, so that $M' = 1/D$.

Eqn. (4) now becomes

$$S/(1-S) = A/D \cdot K + 1/D$$

which yields on rearrangement

$$S = (A + K)/(DK + A + K)$$

When this function for S and the mean value of i are substituted in eqn. (1), the equation

$$T_m = (A + K)N/(DK + A + K) + 0.38 \tag{5}$$

is obtained as a final result.

DISCUSSION OF RESULTS

It is apparent from the graphs used to deduce eqn. (5) that although the calculations of the extraction equilibria are exact, eqn. (5) only represents the simplest approximation to the effects of N, D, K, A and c on the value of T_m, for values of these variables which make $S < 0.8$, when $c \leqslant A/2$. The approximate nature of this equation is possibly due to small effects of the values of c and A which are not apparent in the values of S measured, since these are based on values of T_m estimated by a maximum finding calculation which only uses the three largest concentrations in the data presented to it, and which makes no allowance for the shape of the peak. The error involved by this approximation would only cause a maximum error in the value of S of 0.5%, the actual error in S varying with the shape of the peak.

It has been estimated that when an actual countercurrent extraction is performed, the least error that can be expected in assessing a value of T_m is about 1% of that value, this error being mainly due to incomplete transfer of the aqueous phase after each set of extraction equilibria has been attained.

The validity of the calculations leading to the establishment of eqn. (5) has been tested for every set of data with $c \leqslant A/2$ which gives $S < 0.8$. Fig. 6 graphs the value of T_m after 50 extractions obtained by computer calculations, $T_m(c)$, against the value of T_m calculated from eqn. (5), $T_m(5)$. Several sets of data gave the same point on this graph, and where this has occurred only one point has been inserted.

The maximum value of the difference $|T_m(c) - T_m(5)|$ is 0.3 and the mean value of these differences is 0.1 units.

When eqn. (5) is used with data for which $0.8 < S < 0.95$, and with $c \leqslant A/2$, the mean value of the $|T_m(c) - T_m(5)|$ difference is 0.2, and the maximum value of this difference 0.6. Eqn. (5) can therefore be applied, with a reduced accuracy, to

sets of data for which $0.8 < S < 0.95$, although in the discussion of Fig. 4 the curvature of this graph beyond $S = 0.8$ has been used to limit further curve fitting to data for which $S < 0.8$. This curvature was too large to be neglected, and it must be concluded that there is a compensation for this non-linearity in some later part of the derivation of the final equation. In which part this occurs cannot be determined, since if Fig. 4 is not linear, the further graphs used to establish eqn. (5) cannot be constructed.

These results were calculated for the distribution of halogen and interhalogen compounds between carbon tetrachloride and aqueous solutions of alkali halides, but the results may be generally applied to other systems in which comparable equilibria are obtained.

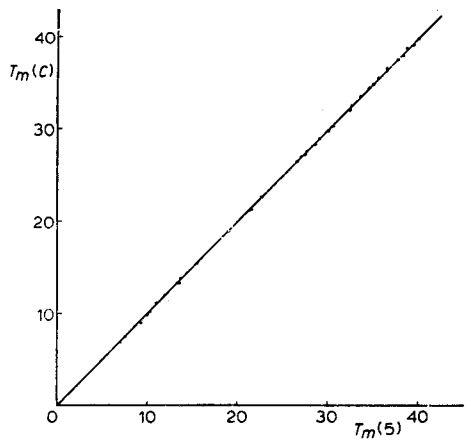

Fig. 6. Comparison of the results obtained by computer calculation, $T_m(c)$, and by the use of eqn. (5), $T_m(5)$, to find the position of the maximum in the distribution of halogen amongst the extraction tubes, after 50 extractions, for various sets of values of D, K, A and c.

ACKNOWLEDGEMENTS

I wish to thank the Mathematics Department of this College for the loan of the computer with which the calculations described in this paper were performed.

SUMMARY

A general relationship between the variables involved in the countercurrent extraction of a solute by the formation of a 1 : 1 complex in the extracting solution has been found. Equations were fitted to the results obtained when an electronic computer was used to calculate the equilibria at each stage of the extraction transfer processes. Combination of these has yielded a final expression of simple form.

RÉSUMÉ

L'auteur a effectué une étude sur l'influence d'un agent complexant lors d'extractions à contre-courant. On a pu établir une expression mathématique simple, en utilisant un compteur électronique pour calculer l'équilibre à chaque stade de l'extraction.

ZUSAMMENFASSUNG

Es wurde eine allgemein gültige Beziehung zwischen den Variablen bei der Gegenstrom-Extraktion eines gelösten Stoffes gefunden, die sich durch eine einfache mathematische Formel ausdrücken lässt.

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LIQUID–LIQUID EXTRACTION OF ZIRCONIUM WITH TRI-*n*-OCTYLAMINE AND DIRECT COLORIMETRIC DETERMINATION WITH XYLENOL ORANGE

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In recent years, it has been recognized that direct non-aqueous colorimetry of trace elements can be very convenient in solving many special analytical problems. The advantages of the direct non-aqueous determination consist mainly in achieving an appreciable increase of concentration of the desired element, due to the great volume reduction obtained by the solvent extraction process, and in avoiding the stripping step which is required when the determination must be carried out in an inorganic phase. Moreover, where a direct organic phase determination is available, the preliminary solvent extraction of the element to be determined from all, or part, of the interfering ions can be a very interesting improvement in the overall analytical method.

Recently, the extractants most widely used in the organic phase determination of elements are tri-*n*-octylphosphine oxide (TOPO) and 2-thenoyltrifluoroacetone (TTA). After extraction with TOPO, uranium has been determined in the organic phase with dibenzoylmethane[1], zirconium with pyrocatechol violet[2], chromium with diphenylcarbazide[3], titanium with thiocyanate[4] and iron with 1,10-phenanthroline[5]. On the other hand, TTA gives complexes which are markedly coloured. Therefore TTA can be used both as the extractant and as the colorimetric reagent. With the use of TTA, chromium[6], uranium[7] and iron[8,9] have been determined in the organic phase.

In the literature, no example was found on the use of tri-*n*-octylamine (TNOA) in organic phase colorimetry. As is well known, TNOA is used extensively because of its selectivity in the extraction of several anionic complexes, and because of its favourable ionic exchange properties[10–15].

Since zirconium is quantitatively extracted by TNOA in a hydrochloric acid medium[11,14,15], it was our aim to study a selective and sensitive method for the organic phase colorimetry of this element.

The specific reagent used was xylenol orange, which had been reported in the literature as a very sensitive and selective reagent for the colorimetric determination of zirconium and hafnium in an aqueous phase[16–18].

EXPERIMENTAL

Equipment and reagents

Spectrophotometric determinations were carried out by means of an Uvispek

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Spectrophotometer, (Hilger Co., London), by using glass optics and glass cells having an optical length of 10 mm.

Liquid–liquid extraction was performed in glass ampoules shaken by an electrically operated wrist-type shaker.

Xylenol orange, whose chemical composition is 3 : 3′-bis-N : N-di(carboxymethyl)-aminomethyl-*o*-cresolsulphonphthalein, was supplied by B.D.H. (London) and tri-*n*-octylamine (TNOA) by Fluka (Buchs S.G., Switzerland).

All the remaining chemicals were of analytical grade. The standard solutions of zirconium were prepared by dissolving zirconium nitrate in concentrated hydrochloric acid and by titrating with EDTA[19].

The xylenol orange solutions (0.05% to 0.4%) were prepared by dissolving the finely powdered reagent in absolute alcohol.

Extraction conditions

TNOA completely extracts zirconium from hydrochloric acid solutions of 9 to 12 *N*.

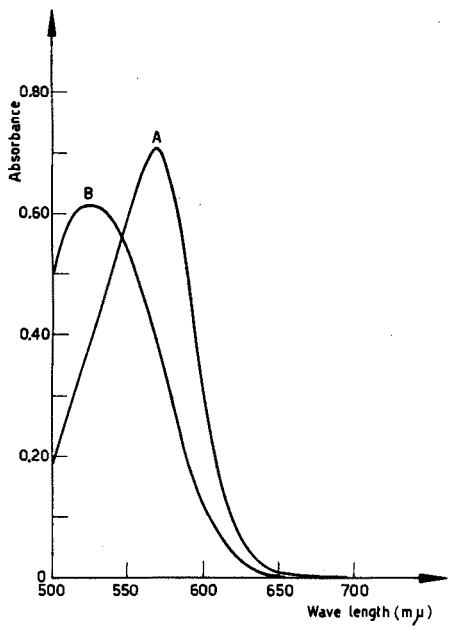

Fig. 1. Absorption spectra of xylenol orange–zirconium complexes. A: (reagent-deficient solution) 400 μg Zr in 5 ml of 0.1 *M* TNOA + 10 ml ethanol + 2.5 ml 0.05% xylenol orange + 2 ml pyridine + ethanol to 50 ml; Blank: reagents only. B: (reagent excess) 100 μg Zr in TNOA and 43 ml 0.05% xylenol orange + 2 ml pyridine; Blank: reagents only.

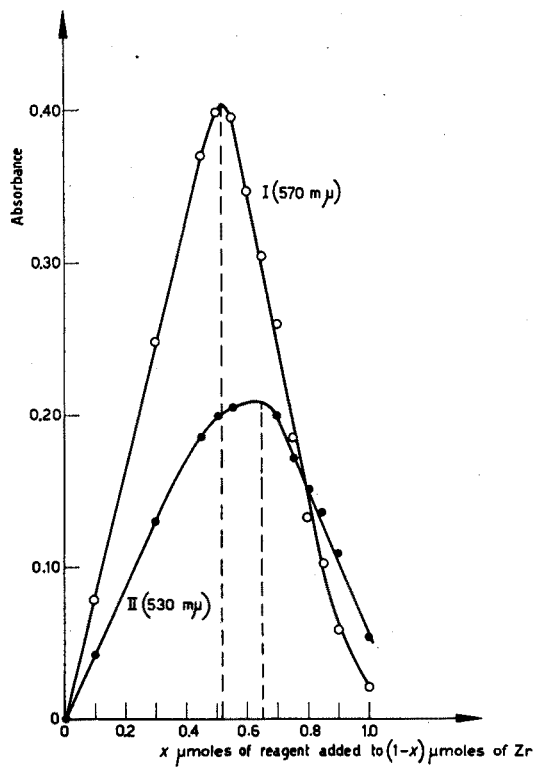

Fig. 2. Determination of molecular ratio of xylenol orange–zirconium complexes. Variable amounts of zirconium (1—*x*) in 5 ml of 0.1 *M* TNOA + 10 ml ethanol + variable amounts of xylenol orange (*x*) + 2 ml pyridine + ethanol to 50 ml. Measurement after 30 min against ethanol at 570 mμ (I) and 530 mμ (II).

Anal. Chim. Acta, 26 (1962) 204–211

From zero to 6 N the extraction does not take place and from 6 to 9 N it is incomplete[11,15]. Therefore, solutions of zirconium in 11 N HCl were used for the extraction with 0.1 M TNOA. 10 ml of the zirconium solution were shaken for 10 min with 7.5 ml of TNOA. After the separation of the two phases, 5 ml of organic solution were directly transferred into a 50-ml glass flask for colorimetry.

Absorption spectra and molecular ratios of complexes

In organic phase colorimetry of zirconium with TOPO–pyrocatechol violet[2], pyridine had been used to buffer the solution. Therefore, pyridine was first tested as buffer in the present work.

The experiments showed that a straight line calibration curve (between 0.1 and 3 μg per ml) and good sensitivity (ε = 27,800 at 530 mμ) can be achieved but the method presents some limitation because of interferences produced with pyridine by ions which give precipitates (U^{+6} and Fe^{+3}) or strongly coloured solutions (Cu^{+2} and Co^{+2}).

Nevertheless, as shown in Fig. 1, it is interesting that two types of complexes have been found in pyridine buffered systems; one type, which gives rise to the absorption peak at 570 mμ, is formed with an insufficient amount of xylenol orange, and the other type, which yields the absorption peak at 530 mμ, is formed with an excess of reagent. The molecular ratio of the two types of complexes was obtained by the method of continuous variations[20,21]. As shown in Fig. 2, at 570 mμ the maximum absorbance corresponds to x = 0.52 which makes $n = x/(1-x) = 1.08$, and at 530 mμ corresponds to x' = 0.67 which makes $n = x'/(1-x') = 2.03$. These values confirm

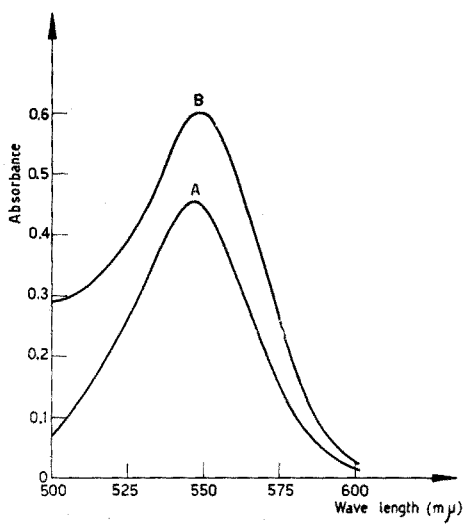

Fig. 3. Absorption spectra of xylenol orange–zirconium complex. A: (reagent-deficient solution) 200 μg Zr in 5 ml of 0.1 M TNOA + 10 ml ethanol + 2 ml 0.05% xylenol orange + 2 ml acetic acid + ethanol to 50 ml; Blank: reagents only. B: (reagent excess) 60 μg Zr in TNOA and 10 ml 0.2% xylenol orange; Blank: reagents only.

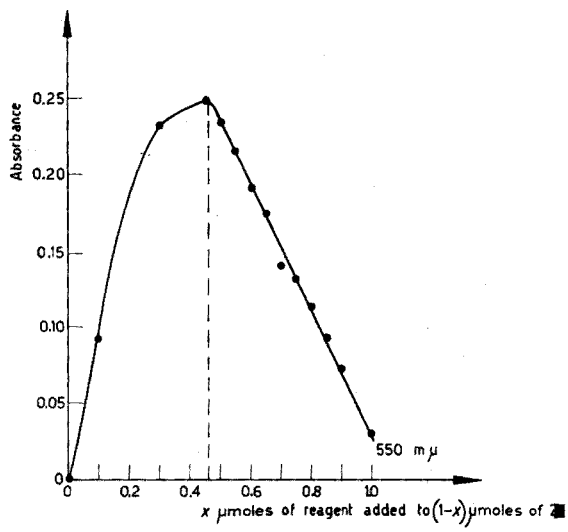

Fig. 4. Determination of molecular ratio of xylenol orange–zirconium complex. Variable amounts of zirconium (1—x) in 5 ml of 0.1 M TNOA + 10 ml ethanol + variable amounts of xylenol orange (x) + 2 ml acetic acid + ethanol to 50 ml. Measurements after 10 min against ethanol at 550 mμ.

that in the organic phase and in the presence of pyridine two different complexes can be formed: the complex ZrX, which is stable when zirconium is in excess and the complex ZrX_2, which is stable with excess of reagent. Analogous behaviour had been already reported for the system zirconium–quercetin[22,23] in which complexes containing one atom of zirconium per molecule of quercetin or one atom of zirconium per two molecules of quercetin can be formed according to the concentration ratio of the two components.

In conclusion, because of the above interfering phenomena, the pyridine buffered organic phase system does not allow such a high selectivity as that claimed by CHENG[16] for the aqueous solution method. Therefore it was decided to investigate the possibility of buffering at an acidic pH value by adding concentrated acetic acid.

In this case, as Fig. 3 shows, a single maximum at about 550 mμ was obtained both with insufficient and with excess reagent. Curve A of Fig. 3 (excess of reagent) was obtained by using a zirconium solution containing 0.66 μmoles of the element (1.2 μg/ml) to which 30 μmoles of reagent (10 ml of 0.2% xylenol orange) were added. Curve B of Fig. 3 (insufficient reagent) was obtained using 2.2 μmoles of zirconium mixed with 1.5 μmoles of reagent (2 ml of 0.05% xylenol orange).

The molecular ratio of the zirconium–xylenol orange complex in an acetic acid medium was determined at 550 mμ by the method of continuous variations. The plot in Fig. 4 shows that the maximum absorbance is obtained at about $x = 0.48$, hence $n = 0.48/(1-0.48) = 0.92$. Therefore the most probable complex composition is ZrX.

COLORIMETRY IN THE PRESENCE OF ACETIC ACID

On the basis of the experiments reported above the acetic acid buffered system appeared to be very promising for the standardization of a reliable method for the organic phase colorimetry of zirconium. Therefore this problem was investigated in detail.

Influence of various parameters and calibration curve

To check for the best sensitivity, increasing amounts of xylenol orange were added

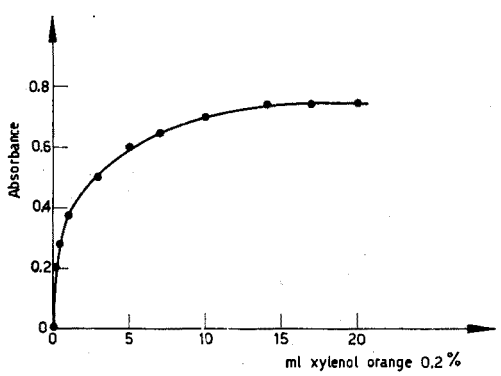

Fig. 5. Effect of xylenol orange added on absorbance. 75 μg Zr in 5 ml of 0.1 *M* TNOA + 10 ml ethanol + variable amounts of 0.2% xylenol orange + 2 ml acetic acid + ethanol to 50 ml. Wave length: 550 mμ. Reference: similar zirconium-free blanks.

to 75 μg of zirconium and then 2 ml of acetic acid were added. Measurements were made at 550 mμ against similar blanks.

The plot in Fig. 5 shows that the absorption plateau is reached at about 20 ml of 0.2% xylenol added.

TABLE I

EFFECT OF THE AMOUNT OF ACETIC ACID BUFFER ON ABSORBANCE

Solution: 5 ml 0.1 *M* TNOA + 75 μg Zr + 10 ml 100% ethanol + 10 ml 0.4% xylenol orange + concentrated acetic acid + ethanol to 50 ml. Wave length: 550 mμ. Reference: zirconium-free solutions of the same composition as each sample

Acetic acid ml	*Absorbance*
0.5	0.82
1.0	0.81
2.0	0.79
3.0	0.78

Thus, to determine the effect of acetic acid on absorbance, a system containing 10 ml of 0.4% xylenol orange in absolute alcohol was used. The effect of the amount of acetic acid added is quite low, as shown in Table I.

The effect on absorbance of standing is reported in Table II. Colour intensity remains stable within 30 min from the addition of reagent and then decreases slowly. Therefore the calibration curve measurements were made 10 min after the addition of reagent.

TABLE II

EFFECT ON ABSORBANCE OF STANDING

Solution: 5 ml 0.1 *M* TNOA + 10 ml ethanol + 10 ml 0.4% xylenol orange + 2 ml concentrated acetic acid + ethanol to 50 ml. Wave length: 550 mμ. Reference: reagents only

Standing (min)	*Absorbance*		
	0.2 μg/ml Zr	*1 μg/ml Zr*	*2 μg/ml Zr*
5	0.120	0.590	1.136
10	0.116	0.590	1.134
15	0.115	0.587	1.134
30	0.114	0.584	1.133
45	0.106	0.565	1.117
60	0.102	0.550	1.102

The calibration curve was obtained under the following conditions: each standard amount of zirconium (2 to 150 μg) was dissolved in 10 ml of 11 *N* hydrochloric acid and extracted with 7.5 ml of 0.1 *M* TNOA. After a 10 min shaking and phase separation, exactly 5 ml of each organic phase were transferred into a 50-ml calibrated glass flask. Such samples therefore contained from 1.33 to 100 μg of zirconium. To each sample were added 10 ml of absolute ethanol, 10 ml of 0.4% xylenol orange,

2 ml of acetic acid and, finally, ethanol to a 50-ml volume. After 10 min, measurements were made at 550 mμ against a similar zirconium-free blank. The calibration curve is a straight line from 0.025 to 2 μg of zirconium per ml and gives the extinction coefficient $\varepsilon = 53{,}300$.

TABLE III

DETERMINATION OF ZIRCONIUM IN THE PRESENCE OF FOREIGN IONS

Initial solution containing 75 μg (0.825 μmoles) of zirconium. Amount of zirconium determined by colorimetry: 50 μg in 50-ml samples

Added metallic ion	*Amount of foreign ion before extraction (μmoles)*	*Ratio of foreign ion to zirconium, before extraction*	*Zirconium found (μg)*	*Error (%)*
None	—	—	50.00	—
Mn^{+2}	82.5	100	50.75	+1.5
Sn^{+2}	82.5	100	50.15	+0.3
Co^{+2}	8.25	10	50.25	+0.5
Bi^{+3}	82.5	100	50.15	+0.3
Cd^{+2}	82.5	100	49.00	—2.0
Pb^{+2}	82.5	100	50.00	0.0
U^{+6}	8.25	10	49.00	—2.0
Fe^{+3}	8.25	10	50.00	0.0
Cr^{+3}	82.5	100	50.10	+0.2
Cr^{+6}	82.5	100	50.25	+0.5
Hg^{+2}	82.5	100	49.00	—2.0
Ti^{+4}	8.25	10	51.50	+3.0
Ce^{+4}	8.25	10	50.50	+1.0
Tl^{+3}	82.5	100	49.50	—1.0
Pt^{+2}	82.5	100	50.50	+1.0
Au^{+3}	82.5	100	49.25	—1.5
Pd^{+2}	82.5	100	51.00	+2.0
Se^{+4}	82.5	100	50.50	+1.0
Zn^{+2}	82.5	100	51.00	+2.0
Nb^{+5}	8.25	10	50.50	+1.0
Ta^{+5}	8.25	10	49.25	—1.5
Ga^{+3}	8.25	10	49.50	—1.0
Th^{+4}	82.5	100	49.75	—0.5
La^{+3}	82.5	100	51.00	+2.0
Cu^{+2}	1.65	2	51.00	+2.0
In^{+3}	82.5	100	49.00	—2.0
Mo^{+6}	8.25	10	51.50	+3.0
W^{+6}	8.25	10	49.00	—2.0
As^{+3}	82.5	100	51.00	+2.0
Th^{+4} [a]	8250	10,000	49.75	—1.0
La^{+3} [a]	8250	10,000	49.75	—0.5
U^{+6} [b]	825	1000	49.25	—1.5
Fe^{+3} [c]	825	1000	49.00	—2.0
Cu^{+2} [d]	8.25	10	48.75	—2.5
$W+V+Mo+Ce^{+4}+Fe$ [e]	412	500	49.00	—2.0

[a] Direct extraction of zirconium from 50 ml of 11 *N* HCl
[b] Preliminary extraction of uranium from 6 *N* HCl with 30 ml of 0.1 *M* TNOA
[c] Preliminary extraction of iron from 4 *N* HCl with 30 ml of 0.1 *M* TNOA
[d] Preliminary extraction of copper from 6 *N* HCl with 10 ml of 0.1 *M* TNOA
[e] Preliminary extraction of the five elements from 4 *N* HCl with 30 ml of 0.1 *M* TNOA

The effect of interferences

Zirconium, when extracted with TNOA from an 11 *N* hydrochloric acid solution, is immediately freed from all the ions that do not form chloride complexes. They are Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Fr^+, NH_4^+, Be^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Ra^{+2}, Mg^{+2}, Sc^{+3}, Y^{+3}, Al^{+3}, Ac^{+3}, Ce^{+3}, Ni^{+2}, Si^{+4}, Th^{+4}, and the whole group of rare earths. Therefore zirconium can be easily determined when the original solution contains one or more of the above-mentioned elements. Furthermore, in the acetic acid buffered system no interference from many of the elements extracted with TNOA takes place.

Several amounts of interfering ions were added to 0.825 μmoles of zirconium (75 μg), and after TNOA extraction, measurements against a similar blank were carried out.

Table III shows that concentrations one hundred times higher than that of zirconium can be tolerated for the following elements: Mn^{+2}, Bi^{+3}, Sn^{+2}, Cr^{+3}, Cr^{+6}, Hg^{+2}, Zn^{+2}, Cd^{+2}, Pb^{+2}, As^{+3}, In^{+3}, Te^{+4}, Au^{+3}, Pt^{+4}, Pd^{+2}, Sc^{+3}, Th^{+4}, La^{+3}. Moreover, ten times higher concentration can be tolerated for Co^{+2}, Fe^{+3}, U^{+6}, Ti^{+4}, Mo^{+6}, Ce^{+4}, Nb^{+5}, Ta^{+5}, W^{+6}. Copper(II) does not interfere provided that it is maintained at a concentration lower than twice that of zirconium.

As shown in Table III, other special cases have been investigated. Good results were obtained in the extraction and determination of zirconium from 50 ml of 11 *N* hydrochloric acid containing thorium and lanthanum at a concentration 10,000 times higher than that of zirconium. To increase the tolerable amounts of the partially interfering elements such as iron, uranium, tungsten, molybdenum, cerium(IV) and copper a considerable improvement can be achieved by previously extracting part of the interfering element from the initial solution. Thus, solutions containing iron or uranium amounts 1000 times that of zirconium were extracted with 30 ml of 0.1 *M* TNOA from 4 *N* or 6 *N* hydrochloric acid solutions respectively. Zirconium was then determined in the usual way within the limit of experimental error. Analogous results were obtained by a pre-extraction of 6 *N* hydrochloric acid solutions containing zirconium as well as 100 times its amount of each of the following ions: W^{+6}, U^{+6}, Mo^{+6}, Ce^{+4}, and Fe^{+3}, or 10 times Cu^{+2}.

Acetic acid and small amounts of nitric acid do not interfere. Sulfuric, perchloric and hydrofluoric acid interfere either by complexing zirconium or by lowering its extraction.

CONCLUSION

The experiments reported above show that in principle the colorimetric determination of zirconium in the organic phase can be carried out either in a pyridine or in an acetic acid buffered system. Nevertheless the former method is practically limited to the case in which zirconium is accompanied by elements that are not extractable by TNOA in the conditions considered. The latter method, which in addition is much more sensitive, is in any case preferable.

By means of the acidic buffer method, a few μg of zirconium can be determined in the presence of large amounts of many other elements.

ACKNOWLEDGEMENT

The authors wish to express their appreciation of the useful laboratory work done by Mr. A. ALBINI.

SUMMARY

A new, very sensitive method for the non-aqueous colorimetry of zirconium is described. Tri-*n*-octylamine solutions obtained by liquid–liquid extraction of Zr from the initial 11 *N* HCl solution are used with xylenol orange as reagent. For pyridine buffered systems a 1 : 1 complex is formed with insufficient reagent and a 1 : 2 complex with excess of reagent. For systems buffered with acetic acid, only the 1 : 1 complex is formed (absorption maximum 550 mμ; ε = 53,300).

The acetic acid method is more sensitive and many foreign ions can be tolerated. Zirconium can be determined in the presence of 10,000 times its amount of non-extractable ions (such as alkali metals, alkaline earths, rare earths, aluminium, etc.) and of 100 or 10 times its amount of many other elements which are extracted by the amine.

RÉSUMÉ

Une nouvelle méthode très sensible est proposée pour le dosage colorimétrique du zirconium en milieu non aqueux. On utilise les solutions de tri-*n*-octylamine, obtenues par extraction liquide–liquide du Zr de la solution initiale (11 *N* HCl) et le xylénol orange comme réactif. Le zirconium peut être dosé ainsi en présence de 10,000 fois sa teneur en ions non extractibles (tels que: métaux alcalins, alcalino-terreux, terres rares, aluminium, etc.), et en présence 100 à 10 fois de nombreux autres éléments extraits par l'amine.

ZUSAMMENFASSUNG

Beschreibung einer colorimetrischen Methode zur Bestimmung von Spurenmengen von Zirkonium nach Extraktion aus wässriger Lösung mit Tri-*n*-octylamin unter Verwendung von Xylenolorange als Reagenz. Die Genauigkeit der Methode wird auch durch grössere Mengen vieler anderer Elemente nicht beeinflusst.

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THE DETERMINATION OF TRACE AMOUNTS OF TOTAL NITROGEN IN PETROLEUM DISTILLATES EXTRACTIVE PERCOLATION METHOD

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INTRODUCTION

An increased insight into the processing and the performance of petroleum products has stressed the role played by trace amounts of nitrogen compounds in oil fractions[1]. There is at present a considerable interest in traces of total nitrogen, even for amounts below 10 p.p.m., occurring in a wide range of petroleum products.

Total nitrogen in petroleum products is most conveniently determined after conversion to ammonia by destructive treatment, and two methods are generally employed for this purpose: the Kjeldahl digestion and the TER MEULEN hydrogenation. However, the extremely low level of nitrogen concentrations now of interest conflicts with the character of such methods, since it is necessary to decompose nearly 100 % hydrocarbon ballast. Although recent papers that have appeared deal with interesting modifications, it must be concluded that Kjeldahl treatment along such lines[2] is not satisfactory owing to high and inconstant blank values caused by the large consumption of reagents. NOBLE's Kjeldahl modification[3] considerably improves this situation by careful purification of ingredients, but a blank of 5–10 p.p.m. was found to remain. KING's modification of TER MEULEN's destructive hydrogenation[4] seems to suffer less from reagent contamination, but involves the handling of minute amounts of ammonia and seems to be limited to samples boiling below 250°.

It was recognized that a more attractive method, suitable for routine application, would be one permitting the use of commercial grade reagents, yet showing a negligible blank and employing a finish not too sensitive to accidental trace contaminations. These requirements call for the use of large samples together with a limited reagent consumption, conditions fulfilled, in principle, by a concentration of the nitrogen compounds from a large sample prior to analysis.

A method presenting some of the above features was proposed by WANKAT AND GATSIS[5]. Here, 0.5- to 1-l samples are catalytically hydrogenated at a high pressure in a heated rotating autoclave and the ammonia formed is fixed on acidic alumina. Besides its extreme slowness, we found other disadvantages with this method such as its unsuitability for samples in the gas-oil boiling range and a "memory effect" which made results dependent on the nitrogen level in previous runs.

Preconcentration of the organic nitrogen compounds by percolation of a large sample through silica gel was applied by BOND AND HARRIZ[6], using a long narrow column. Final analysis was done by subjecting the column, after breaking it into pieces, to Kjeldahl treatment. This method, however, apart from giving trouble in the decomposition step because of the silica gel in the digest, appears to be very slow because of the limited percolation rate (10–20 ml/h). SCHLUTER[7] used the same principle of preconcentration, but applied the TER MEULEN hydrogenation for converting the nitrogen compounds into ammonia, making use of a column small enough to be inserted entirely into the hydrogenation apparatus.

Another type of preconcentration is based on the fact that all nitrogen can be removed from petroleum by extraction with concentrated sulphuric acid[1,8]. MILNER *et al.*[9] in 1958 reported the results obtained by a method of this type.

Independently of these authors we found some years ago that a simple extraction as suggested by these authors has a limited application range and in many cases covers only 90% of the nitrogen present in the oil. A novel and more effective preconcentration of nitrogen compounds was therefore developed which is applicable to a wide range of petroleum products and is based on extractive percolation of the oil sample through sulphuric acid on a carrier in a small column. Final analysis is made after Kjeldahl treatment of the column contents. Pumice, used as the inert carrier, proved to have no effect on the Kjeldahl step.

DEVELOPMENT OF THE METHOD

General aspects of sulphuric acid treatment with respect to total nitrogen determination

It has long been known that treatment of an oil sample with dilute mineral acids can cause an appreciable amount of the nitrogen compounds present to be removed; a division of these compounds into a basic (removed) and a non-basic (retained) portion was thus generally made*. The latter portion is difficult to isolate. This is one of the reasons why the present knowledge of non-basic nitrogen compounds lags behind that of the basic ones, although in many petroleum products the former

TABLE I

EXTRACTION OF NON-BASIC NITROGEN COMPOUNDS BY 98% SULPHURIC ACID

Nitrogen compound added	*Dissolved in*	*Nitrogen present p.p.m.*	*Nitrogen found*			
			1st extraction		*2nd extraction*	
			p.p.m.	*Recovery %*	*p.p.m.*	*Total recovery %*
Pyrrole	isooctane	95	91	96	nil	96
Indole	isooctane	102	106	103	nil	103
			104	102	nil	102
2,3-Dimethylquinoxaline	isooctane	100	105	105	nil	105
			104	104	nil	104
Carbazole	benzene	73	66	90	9	103
			55	75	20	103

* More recently, basic nitrogen compounds have been defined as compounds which can be titrated with perchloric acid in a non-aqueous medium such as a 50:50 solution of glacial acetic acid and benzene. Since indoles, some pyrroles and carbazoles cannot be titrated in it, they are considered non-basic, whilst pyridines, quinolines, isoquinolines and some substituted pyrroles can be titrated and are thus considered basic compounds[10].

definitely predominate[10]. Some authors, however, state that 98% sulphuric acid is capable of removing all the nitrogen compounds from an oil[1,8]. Although this treatment generally cannot serve for identification purposes because of the chemical attack by the acid, it is quite interesting from a view-point of concentrating traces of nitrogen compounds from oil samples.

A study was therefore made on how far shaking with a small quantity of 98% sulphuric acid can remove nitrogen compounds from mixtures with hydrocarbons. The above statements[1,8] that all the nitrogen can thus be removed were confirmed. This is shown in Table I for a number of typical non-basic nitrogen compounds (synthetic solutions) and in Table II for oil samples, by Kjeldahl analysis of the acid concentrates obtained. The extractions were carried out on 20-ml portions of test solution using 0.2 ml of concentrated acid each time. The oil samples were diluted with a tenfold volume of petroleum spirit before extraction.

TABLE II

EXTRACTION OF TOTAL NITROGEN FROM OIL SAMPLES BY 98% SULPHURIC ACID

Product	*Basic nitrogen*[a] *p.p.m.*	*Total nitrogen*[b] *p.p.m.*	*Nitrogen recovered by single sulphuric acid extraction*	
			p.p.m.	*recovery*[c] *%*
Straight-run heavy gas oil	96	211	218	103
			216	102
Catalytically cracked cycle oil	31	192	201	105
			186	97

[a] By perchloric acid titration of the type mentioned in the footnote on p. 213.
[b] By direct Kjeldahl determination, using purified reagents[3]
[c] Based on total nitrogen values

This preliminary investigation indicated that a percolation treatment through acid would be satisfactory, for this promised (*a*) maximum extraction efficiency, (*b*) applicability to gas oil and lubricating oil samples in the undiluted state, and (*c*) the treatment of much larger samples.

Extractive percolation

Several potential carriers for sulphuric acid were examined, such as small glass beads, glass wool, glass powder, potassium sulphate and combinations of these.

The most promising results were obtained with fine grade pumice. This material was uniformly wetted with acid by mixing. An additional layer of filtering material proved necessary to avoid any residual acid sludge entrainment. Short-fibred asbestos, used in a small layer, was the most useful of many materials tried for this purpose. However, since the capacity of any filtering pad will depend on such variables as (*1*) the amount and type of the reaction products formed (character of sample), (*2*) the amount of sample passed through, (*3*) the rate of percolation, and (*4*) the quantity of active material in the column, a tentative investigation was made into this matter. Experiments carried out with a column and a filtering pad of the dimensions given in the experimental part (*cf.* Fig. 2) indicated that a minimum length of 5 cm of active

material was necessary to prevent losses of nitrogen concentrate due to entrainment under severe conditions (*i.e.* using a gas oil sample known to be heavily attacked by sulphuric acid, applying the maximum scheduled sample size of 250 ml and a percolation rate of 250 ml/h).

Hence, bed lengths of 7 cm (20 g of percolation material) were used in the work reported here. The effect of the percolation rate was not closely investigated and although experiments made on gasoline samples suggested that much higher rates can be tolerated, a further study was not considered necessary because of the limitations imposed by the viscosity of higher boiling fractions.

The effectiveness of the percolation is demonstrated in Table III by reference to a number of dilutions of typical nitrogen compounds in straight-run light gas oil to a

TABLE III

APPLICATION TO LOW NITROGEN SYNTHETIC BLENDS

Sample: Straight-run light gas oil[a] with nitrogen compounds added as indicated. Sample size: 250 ml

Compounds added (equivalent amounts of)	*Nitrogen added p.p.m.*	*Net nitrogen found p.p.m.*	*Recovery %*
Indole	3.10	3.07	99
Carbazole		3.13	101
2,3-Dimethylquinoxaline			
Tetra-hydroquinoline	3.33	3.38	101
3-Methyl-α-benzindole		3.37	101
Thionaphthoquinoline-(2,3,3′,2′)			

[a] Natural total nitrogen content by this method 1.94 p.p.m.

TABLE IV

APPLICATION AT HIGHER NITROGEN LEVELS

Sample	*Nitrogen found by percolation, p.p.m.*			*Approximate nitrogen indicated by direct Kjeldahl p.p.m.*
	250-ml sample	*50-ml sample*	*25-ml sample*	
Heavy gas oil	227		229	236
	206		232	
	233		231	
	222		232	
Treated cat. cracked gasoline	24.0	24.7[a]		22
	23.7	24.8[a]		
	23.8	24.6[a]		
	24.0	24.6[a]		
Synthetic gasoline	26.5	26.2[a]		26.9[b]
(containing nearly equivalent amounts of	25.9	25.3[a]		
pyridine, pyrrole, indole, carbazole and	26.5	26.1[a]		
2,3-dimethylquinoxaline)	25.6	25.9[a]		

[a] Ammonia titration with 0.01 *N* acid; otherwise 0.05 *N* acid

[b] Calculated for synthetic sample

3-p.p.m. level. The precision as well as the accuracy are of a very high order. Blank values amounted to approximately 0.7 p.p.m. with variations of less than 0.1 p.p.m. including the pumice reagent and using commercial grades of sulphuric acid and potassium sulphate in the Kjeldahl treatment.

The high degree of precision and accuracy demonstrated prompted the evaluation of the percolation method at higher nitrogen levels. Table IV presents some results obtained on natural and other samples using various sample sizes. As far as column capacity is concerned a sample of 250 ml at a 200-p.p.m. level seems just on the borderline, but the values found indicated that very precise results could be expected from much smaller samples.

Kjeldahl digestion

It is now generally accepted that the Kjeldahl digestion principle is satisfactory for nitrogen determinations in petroleum products. Studies by BELCHER[11], LAKE *et al.*[12] and MCKENZIE *et al.*[13] have shown that the point of clarification of a Kjeldahl reaction mixture by no means offers a criterion for completeness of the nitrogen conversion. Moreover, it has been shown that afterboil temperatures much above the sulphuric acid boiling point are required to bring the conversion rate for refractory nitrogen compounds in petroleum between acceptable limits. Temperature elevation is most generally effected by adding potassium or sodium sulphate. A critical examination showed that an afterboil period of 1½ h at 380° was necessary (360° was found to act too slowly and 400° caused significant nitrogen losses due to thermal decomposition of ammonium sulphate). Hence, control of the salt/acid ratio is most important. Since, however, the amount of acid present in the final stage (afterboil) is determinative, one has to correct for the acid portion consumed during the destruction of the sample.

TABLE V

VARIATION IN SULPHURIC ACID CONSUMPTION AND ITS EFFECT ON THE AFTERBOIL TEMPERATURE IN KJELDAHL DIGESTIONS

(Method: 2 g sample, 30 ml sulphuric acid, 0.25 g catalyst mixture, 20 g anhydrous sodium sulphate)

Sample	*Observed sulphuric acid consumption ml/g*	*Afterboil temperature °C*
Cracked distillate[a]	3.4	355
Heavy gas oil	7.0	366
Asphaltic bitumen	10.2	385

[a] Initial boiling point 85°; 50% boiling below 320°

MIDDLETON AND STUCKEY[14], dealing with pure compounds, added an extra amount of acid at the commencement of the digestion, equalling that consumed by the compound under test. The amount of additional acid required is obtained from the formula of the substance by a simple calculation. This is impossible with petroleum samples and, moreover, an additional effect is produced by the sample volatility, as a result of which uncontrolled hydrocarbon quantities are boiled off without making

demands on the acid. Table V illustrates the magnitude of these effects on the afterboil temperature when one standard initial salt/acid ratio is applied.

A simple way of ensuring the correct afterboil temperature with petroleum samples appeared to be the estimation of the amount of acid present in the digestion flask by weighing after the clearing of the reaction mixture. To this end a somewhat different digestion procedure is followed in which the initial charring of the sample is effected without the addition of salt (*i.e.* with acid and catalyst only).

Somewhat unexpectedly the omission of salt resulted in a considerable reduction (by one hour or more) of the period necessary to clear the mixture and caused much less foaming than in the conventional digestion process. A typical example is presented in Fig. 1.

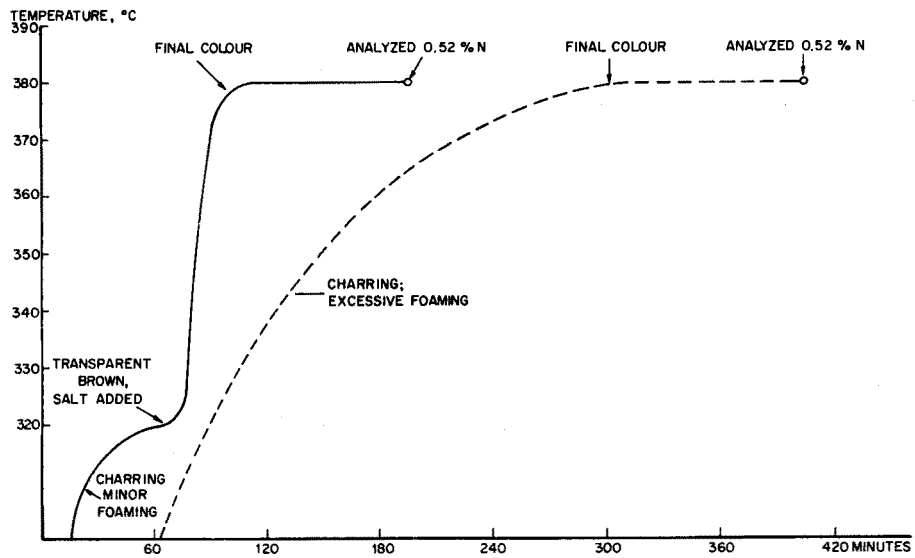

Fig. 1. Comparison of Kjeldahl digestion styles. Sample: 2 g of asphaltic bitumen. Conditions: 40 ml sulphuric acid, 250 mg catalyst mixture. - - - - conventional digestion style; —— proposed digestion style.

A similar practice was followed in the present work. Here, the motives were even more pressing than in straight Kjeldahl digestions, since the amount and the character of the organic matter retained in the column may vary widely. No interference was noticed in the Kjeldahl digestion from the pumice particles, except that the amount of acid present in the pumice pores takes no real part in the boiling process. This fact is incorporated in the salt weight formula given in the method; the multiplication factor 0.72 was derived from literature data on boiling-point elevations of sulphuric acid by potassium sulphate[14]. This salt was preferred to anhydrous sodium sulphate on account of its better solubility. The all-glass Parnas-type apparatus for steam-distilling the ammonia, as used in this work was found to present a maximum of safe handling, to exclude bumping, and to reduce the carry-over of caustic soda spray to a negligible amount.

METHOD

Apparatus

Percolation column, glass, (Fig. 2) with a loose perforated porcelain disc.

Separating funnel, 250-ml capacity, the stem provided with a conical ground joint 24/25 to fit on the column.

Kjeldahl flasks, 300-ml capacity.

Digestion stand, consisting of a tripod carrying a hard asbestos plate with a 50-mm hole in the centre. Provision should be made for clamping the flask at an angle of 30° with respect to the horizontal. Any convenient extension may be made in this apparatus to suit multiple determinations.

Distillation apparatus, all-glass, Parnas type, with detachable distillation flask (Fig. 3).

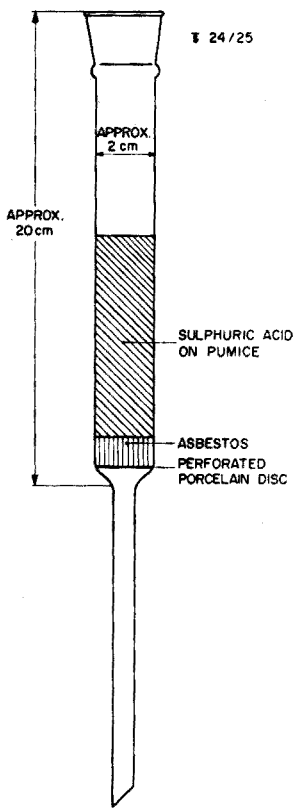

Fig. 2. Percolation column.

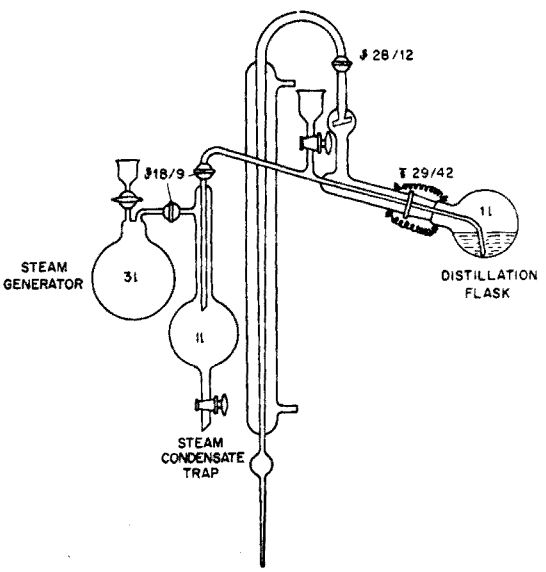

Fig. 3. Distillation apparatus.

Reagents

Asbestos, A.R., short-fibred grade. The British Drug Houses' M.A.R. grade is satisfactory.

Boric acid solution, 4% A.R. Add so much 0.1 *N* sodium hydroxide solution that 30 ml of the 4% solution upon dilution with 120 ml of distilled water and addition of

5 drops of Tashiro indicator (see below), yields a colour intermediate between green and violet. Store in a polyethylene bottle.

Catalyst mixture, prepared by mixing anhydrous copper sulphate, powdered selenium and mercuric oxide in a ratio of 1:1:2 by weight.

Pumice, A.R. Prepare a 25–50 mesh fraction by screening. Boil 500 g of the pumice fraction twice in 1.5-l portions of distilled water for half an hour, filter and dry for two hours at 500°.

Sulphuric acid, 98%, A.R. (sp.gr. 1.84).

Sulphuric acid on pumice. A quantity sufficient for about 40 determinations is prepared in the following way: mix 250 ml of 98% sulphuric acid with 500 g of pumice and shake until a uniformly wetted product is obtained. Store in bottles with polyethylene-lined covers.

Tashiro indicator, prepared by dissolving 0.125 g of methyl red and 0.083 g of methylene blue in 100 ml of ethyl alcohol.

Percolation

Weigh the required amount of sample (Table VI) into the separating funnel. Mount the dry percolation column on a 500-ml suction flask and put in the perforated porcelain disc. Introduce into the column 0.75 g of asbestos, and compact it into a pad

TABLE VI

SAMPLE SIZE AND PRECISION SCALE

Expected nitrogen content p.p.m.	*Approx. sample size g*	*Approx. magnitude of blank*[a] *p.p.m.*	*Precision*[b] *p.p.m.*
0–20	200	0.7	5% of amount present (not better than 0.2 p.p.m.)
20–50	100	1.5	2
50–100	50	3	3
100–200	25	6	5

[a] Expected maximum variation *ca.* ± 10%

[b] Defined as the maximum acceptable difference between duplicate results by the same operator

10 mm thick. Add 20.0 g of sulphuric acid on pumice (see Fig. 2). Ensure a uniform filling by tapping against the wall of the column and by slightly compressing the surface of the pumice. Connect the separating funnel to the column. The sulphuric acid/pumice reagent is hygroscopic. Moisture take-up should be prevented as far as possible during the above manipulations.

Add the sample as a rapid stream to the column until the liquid has reached a level about 1 cm above the surface of the pumice. From then on percolate the sample at a rate of 4 ml/min, maintaining the liquid level over the surface of the pumice. If necessary apply suction. After the sample has been percolated, wash the separating funnel and column contents with 20 ml of nitrogen-free isooctane. Transfer the contents of the column with the aid of 80 ml of sulphuric acid to a dry Kjeldahl flask previously weighed to the nearest 0.1 g. (Use 100 ml of acid in the case of heavy oils).

Viscous samples may require some dilution with a nitrogen-free diluent such as isooctane to improve flow.

Some cracked products may give rise to considerable heat development when passing through the column. This is of no consequence unless so much heat is developed that gas bubbles destroy the uniformity of the column packing. In that case apply the following pretreatment: Weigh the sample into a dry Kjeldahl flask previously weighed to the nearest 0.1 g. Add 1 ml of concentrated sulphuric acid, shake for 3 min and decant into the separating funnel. Continue in the normal manner described above, using the pretreated sample, and transfer the contents of the column after percolation to the Kjeldahl flask used.

Digestion

Transfer 250 mg of the catalyst mixture to the weighed Kjeldahl flask. Place the flask at an angle of 30° to the horizontal on the digestion stand. Heat at first with a small flame to prevent foam from entering the neck of the flask. Occasionally swirl the flask during heating and bring to the boil as quickly as possible. Continue boiling until the contents of the flask turn a yellowish brown. In the early stages of the digestion an apparently dry spongy carbonaceous cake may be formed. In that case add enough sulphuric acid to keep a bottom of liquid in the flask. Allow to cool and weigh the flask to the nearest 0.1 g. Add potassium sulphate (A.R.) in an amount A, given by:

$$A(\text{g}) = (\text{weight of residual liquid in flask (g)} - 21)\ 0.72.$$

Bring to a full boil, at which point a temperature of 380° will be established. Continue boiling for 90 min, with occasional swirling to keep all the pumice in the boiling acid. Allow to cool, but before the sulphate begins to crystallize dilute with a five-fold quantity of distilled water. Allow to cool further and add two drops of 40% ferric chloride solution slightly acidified with hydrochloric acid.

Distillation

Steam out the distillation apparatus for at least 30 min by heating the steam generator with a blast burner and closing all stopcocks. The steaming-out should be repeated each day before the first distillation. Clean the inner condenser tube as soon as traces of greasy deposits are observed.

Stop heating and open all stopcocks. Disconnect the distillation flask and quantitatively add the contents of the Kjeldahl flask. Connect to the distillation apparatus. Place in a tall 250-ml beaker 30 ml of boric acid solution and 5 drops of Tashiro indicator. Place the beaker under the condenser so that the condenser tip is immersed in the solution. Add so much 40% sodium hydroxide (A.R.) solution through the funnel that a brown precipitate is formed in the distillation flask; then add 20 ml of the sodium hydroxide solution in excess. Wash the funnel with some distilled water.

Caution: The sodium hydroxide solution must be added in small portions, each portion being mixed with the acid solution by blowing through the steam condensate trap. Use a safety trap (suction flask) in the blowing line to catch any liquid forced back.

Close all stopcocks and start the distillation. Continue until the total volume of

liquid in the beaker is about 150 ml. Prevent the distillate from coming over warm; a suitable distillation rate is 5 ml/min. Remove the beaker from the condenser. Discontinue the distillation and open the stopcock of the funnel. Remove the distillation flask and discard the contents.

Titration

Titrate the contents of the beaker with 0.01 or 0.05 *N* hydrochloric acid to the same green-violet end-point as described under *Reagents* (boric acid solution). Use 0.01 *N* acid if the amount of nitrogen expected is below 1 mg; use 0.05 *N* acid above this amount.

Blank

Carry out a blank determination with the same amounts of sulphuric acid on pumice, asbestos, sulphuric acid, catalyst mixture and adding 5 ml of isooctane. Carry out the digestion, distillation and titration exactly as described.

RESULTS AND DISCUSSION

Application of the proposed method to a variety of oil products ranging from gasoline

TABLE VII

APPLICATION OF PROPOSED METHOD TO SAMPLES FROM PRACTICE. COMPARISON WITH METHODS TRIED EARLIER

Product	*Basic nitrogen*[a] *p.p.m.*	*Total nitrogen p.p.m.*			*Proposed method*
		Direct Kjeldahl		*UOP Autoclave hydrogenation*[d]	
		hypobromite finish[b]	*alkalimetric finish*[c]		
Straight-run naphtha	1	4; 0	—	—	0.47
		6; 2			0.59
Cat. cracked gasoline	40	47	47	41	43.5
		51		43	43.1
Power kerosine	3	0	—	0.9	1.49
		0		1.0	1.39
Jet fuel	4	2; 5	—	5.4	4.79
		8; 5		5.0	4.78
Kerosine distillate, 140–250°	—	5	7	—	3.36
		9			
Straight-run gas oil	3	—1	—	1.1	1.94
		1		1.6	1.94
Cat. cracked cycle oil	31	207	187	176	194
		215	197	155	193
Heavy straight-run gas oil, initial b.p. 255°	96	236	215	152	217
		223	207	134	213
Lubricating oil distillate	5	26	—	37	44.6
		32		42	44.9[e]

[a] Electrometric perchloric acid titration method
[b] "NOBLE" — purified reagents[3]; improved destruction; sub-micro ammonia titration with hypobromite and thiosulphate[15]; blank 12 ± 3 p.p.m.
[c] "NOBLE" — purified reagents[3]; improved destruction; ammonia titration with 0.01 *N* acid; blank 7 ± 3 p.p.m.
[d] WANKAT AND GATSIS[5]
[e] 2:1 oil-isooctane dilution

to lubricating oil (Table VII) demonstrates its superiority to earlier methods, including direct kjeldahlization and autoclave hydrogenation. Basic nitrogen figures are also included in the table. Although they are given for orientation only, they illustrate earlier findings that the ratio of basic to non-basic nitrogen in oil samples may vary widely. The results confirm that the proposed method permits a sharp differentiation between total nitrogen values even in a range below 10 p.p.m. and maintains a similar degree of precision and accuracy in higher nitrogen ranges. A scale for optimum sample sizes and precision values (Table VI) could be drawn up on the basis of a large number of determinations. Approximate blank values are included which are to be anticipated at different nitrogen levels (sample sizes). No systematic attempts have been made to apply the method to a nitrogen range much above 200 p.p.m., since here straight Kjeldahl treatment of the sample is satisfactory. However, it is felt that the present principle could also be extended to a still higher nitrogen range if the need for a greater precision should arise. Likewise, it would be possible to extend the method into the parts-per-billion range, if desired, by simply increasing the amount of material percolated. The fact that in the case of gasoline or kerosine there is but a very small attack of the acid bed would render this possible.

The high degree of accuracy exhibited by the method is a direct result of the intimate contact between the acid and the sample, realized by the percolative treatment. This was once more demonstrated on the lubricating oil sample (Table VII, last row), where manual sulphuric acid treatment in gasoline dilution detected only 36 p.p.m. of nitrogen. It was, in fact, believed that the total nitrogen content of this oil was 36 p.p.m. until the present method revealed 45 p.p.m. Later it was found that by repeated manual shaking an additional quantity of 9 p.p.m. could be recovered.

ACKNOWLEDGEMENT

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SUMMARY

A new method is presented for the determination of trace amounts of total nitrogen in petroleum distillates ranging from gasolines to lubricating oils. The method is based on percolation of the sample through concentrated sulphuric acid distributed on a carrier. Owing to its high precision the proposed method allows a sharp differentiation between nitrogen contents even at levels below 10 p.p.m. Factors which commonly interfere with the detection of traces of nitrogen are minimized. The relative simplicity of the method makes it suitable for routine application.

RÉSUMÉ

L'auteur présente une méthode nouvelle pour doser des traces d'azote total dans les distillats de pétrole compris dans l'intervalle entre les essences et les huiles lubrifiantes. La méthode se base sur la percolation de l'échantillon à travers de l'acide sulfurique concentré réparti sur la surface d'un support inerte. Grâce à sa haute précision la méthode proposée permet une différenciation nette entre les teneurs d'azote, même au-dessous de 10 p.p.m.

ZUSAMMENFASSUNG

Beschreibung einer neuen Methode zur Bestimmung von Spurenmengen Gesamtstickstoffs in Erdöldestillaten im Bereich von Benzinen bis Schmieröle. Die Methode beruht auf Perkolation der

Probe durch konzentrierte, auf einem Träger verteilte Schwefelsäure. Die grosse Schärfe des vorgeschlagenen Verfahrens ermöglichen Differenzierung zwischen Stickstoffgehalten selbst bei Konzentrationen unterhalb 10 Teile per Million.

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SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE IN HUMAN PLASMA AND RED CELLS WITH BENZOHYDROXAMIC ACID

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The purpose of this investigation was to develop a spectrophotometric method for the determination of manganese in human plasma and red cells, using benzohydroxamic acid as the color producing reagent. Manganese(II) reacts with benzohydroxamic acid in ammoniacal medium, forming a stable reddish-brown complex. The sensitivity of the color reaction at 500 mμ is 0.015 μg Mn/cm^2 for log I_0/I = 0.001 and Beer's law is obeyed up to 1 p.p.m. in 10-cm cells.

The samples of plasma and red cells are dry-ashed and the mineral constituents are then converted to chlorides with hydrochloric acid. Iron, cobalt and copper are removed by ion exchange because they interfere in the color reaction. The manganese is determined spectrophotometrically in 10-cm cells at a wavelength of 500 mμ.

The accuracy and precision of the method were demonstrated by values obtained for synthetic samples. The recovery of manganese added to split samples was quantitative. Average concentrations of manganese in normal human plasma and red cells are about 0.1 and 0.2 p.p.m., respectively.

EXPERIMENTAL

Apparatus

A Beckman Spectrophotometer, Model DU, equipped with matched 10-cm Corex cells was used.

An Applied Research Laboratories, 2-meter grating spectrograph was employed to examine reagents for contaminants. It was modified with exterior optics and igniter as described by THIERS AND YOE[1]. The excitation source was a direct current arc and the spectra were recorded on 35 mm spectrographic film (Kodak S.A. no. 2). The spectral lines of the elements were located and identified by means of an ARL film projection comparator-densitometer.

Ion exchange columns. The columns were made from 7-mm (o.d.) Pyrex tubing attached to a capillary stopcock on one end and the other end was attached to a 15-cm length of 15-mm Pyrex tubing which serves as a reservoir. The anion exchange resin (Dowex-1, 8X, 50–100 mesh) was added to the column in the form of a slurry and the resin bed was supported on a glass wool plug. The length of the resin bed was 18 cm.

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The "dead" volume of the column was determined by elution of nickel chloride solution with dilute hydrochloric acid and testing the effluent with dimethylglyoxime.

Evaporator cover. Evaporations were carried out under a glass cover to which a side arm had been fitted and through which filtered air was blown. Heat was supplied by infrared lamps and a hot-plate.

Reagents

Hydrochloric acid. Hydrochloric acid of high purity was prepared by two methods: by distillation of the constant boiling mixture and by dissolving pure anhydrous hydrogen chloride gas in triply-distilled water. Acid prepared by both methods proved to be satisfactory for our purpose.

Nitric acid. Nitric acid was purified by distillation; however, the last traces of copper and magnesium are difficult to remove.

Hydroxamic acid reagent. Prepare a 2% w/v solution by dissolving benzohydroxamic acid in water.

Manganese(II). Prepare a standard stock solution by dissolving Matthey's "spec-pure" Mn_3O_4 in hydrochloric acid and diluting to volume. Alternatively, a stock solution may be prepared from electrolytic manganese metal of high purity (>99.9%).

"Reagent grade" ammonium hydroxide was used.

Sampling procedure

Draw the blood sample as described by THIERS *et al.*[2]. Transfer immediately to a 60-ml polyethylene bottle and separate it into plasma and red-cell fractions by centrifugation. After separation, puncture the polyethylene bottle with a platinum–ruthenium hypodermic needle about 1/4 in. above the red-cell layer and draw off the plasma with a clean syringe, taking care not to disturb the red-cells. Transfer the plasma to a clean polyethylene bottle and cap tightly. Draw off the interface between the plasma and red cells (mostly white cells) and discard it. Mix the individual fractions thoroughly before weighing out samples for analysis.

Analytical procedure

Weigh out the samples into platinum dishes (about 10 g for red cells and 20 g for plasma) and dry under the evaporator with the infrared lamp only. When the samples are dry (8 to 10 h), turn on the hot-plate and continue heating until they are charred. This requires about 24 h at a hot-plate temperature of 300° ± 20°. Transfer the charred samples to a muffle furnace heated at about 400°, slowly raise the temperature to 475° (see note *1*) and continue heating until all the organic matter is destroyed (see note *2*).

After ashing, dissolve the inorganic residue in dilute hydrochloric acid and transfer the solution to a small polyethylene beaker. Remove the excess water and acid by evaporation; continue the evaporation until the alkali chlorides just begin to precipitate. Add 2 ml of 12 *N* hydrochloric acid and allow the sample to cool. Filter off the alkali chlorides on a fritted glass crucible and wash thoroughly with 12 *N* hydrochloric acid (see note *3*). Evaporate the acid solution almost to dryness and take up in 1 ml of 12 *N* hydrochloric acid. Transfer this solution to a previously conditioned ion-exchange column. After the solution passes down into the glass wool plug at the top of the column, wash the polyethylene beaker with two 1-ml portions of 12 *N* acid

and add these to the column in sequence. Rinse the beaker with 2 ml of 6 *N* hydrochloric acid, adding it to the column when the last 12 *N* fraction has passed down into the glass wool plug. Complete the elution with 5 additional 2-ml portions of the 6 *N* acid. Discard the first 4 ml of effluent and collect the remaining 10 ml which contain the manganese.

Evaporate the solution to dryness in order to eliminate the large amount of hydrochloric acid. Dissolve the residue in 4 to 5 ml of water, add 0.5 ml of 2% w/v benzohydroxamic acid reagent, 1 ml of concentrated ammonium hydroxide and dilute to 35 ml (see note *4*). Measure the absorbance at 500 mμ in a 10-cm cell against a reagent blank and determine the manganese concentration from a Beer's law graph, prepared from synthetic samples containing known amounts of manganese.

Notes

(*1*) Care must be exercised when the samples are transferred to the muffle furnace. If the temperature is higher than about 400°, the samples will foam vigorously and may overflow the container.

(*2*) If there is a slight amount of carbon left after heating in the muffle furnace, it can be destroyed by heating with a little nitric acid and hydrogen peroxide.

(*3*) The alkali chlorides are removed because they interfere in the ion-exchange separation, due to their low solubility in concentrated hydrochloric acid. Do not attempt to dissolve a dry sample directly in 12 *N* hydrochloric acid and filter off the salts, because they will contain trapped impurities. If the sample is first dissolved in dilute acid or water and the precipitation carried out as directed, the precipitate will contain no manganese.

(*4*) Most of the magnesium and calcium is removed in the first 4 ml of effluent from the ion-exchange column; however, if the removal is incomplete, a slight precipitate may appear when the ammonium hydroxide is added. If the solution appears cloudy at this step, centrifuge until water-clear before making the absorbance measurement.

DISCUSSION OF THE METHOD

Extraordinary care was taken to prevent contamination. All reagents were tested for manganese, spectrochemically. The samples were kept covered in order to avoid airborne contamination, except for brief periods when certain manipulations were necessary. The platinum dishes used for ashing the samples were found to be spectrographically free of manganese. All equipment which came in contact with the samples or reagents was scrupulously cleaned. The blood samples were drawn from the donors by the method described by THIERS *et. al.*[2], using 50-ml hypodermic syringes and platinum–ruthenium needles.

The manganese–organo complex is reddish brown and has a fairly wide absorption band at 500 mμ. At this wavelength, the complex obeys Beer's law up to a concentration of 1 p.p.m. in 10-cm cells. The absorbance of the reagent is negligible; however, reagent blanks were used because of the very small amounts of manganese being determined. The maximum absorbance of the Mn–organo complex is not dependent upon the ammonium hydroxide concentration, provided that enough is added to ensure a pH of 10 or higher. Hence, no buffer is required. Ammonium hydroxide concentrations of up to 7 *M* have no adverse effect on the complex. The ammonia con-

centration does affect the rate of color formation; however, the amount given in the analytical procedure will effect complete color formation in 2 to 3 min. For a more detailed discussion of the benzohydroxamic acid method for manganese, see MILLER AND YOE[3].

The ion exchange separation is an adaptation of the method of KRAUS AND MOORE[4].

RESULTS

The results of analyses of synthetic red-cell samples and of human plasma and red cells are summarized in Tables I, II and III, respectively. The composition of the synthetic red-cell ash is shown in Table IV.

TABLE I

ANALYSIS OF SYNTHETIC RED-CELL ASH

Sample[a] No.	*Mn added p.p.m.*	*Mn found p.p.m.*	*Deviation p.p.m.*
1	0.080	0.080	0.000
2	0.080	0.080	0.000
3	0.080	0.078	—0.002
4	0.080	0.082	+0.002
5	0.080	0.085	+0.005
6	0.080	0.082	+0.002
7	0.080	0.080	0.000
8	0.080	0.078	—0.002

[a] All samples contained 10 g of synthetic red-cell solution and the results are recorded as w/v concentrations.

TABLE II

ANALYSIS OF HUMAN PLASMA

Sample No.	*Sample weight g*	*Mn added µg*	*Mn foud µg*	*Mn found p.p.m.*
345P-1[a]	9.9	8	8.50	
345P-2[a]	10.0	0	0.88	0.09
346P-1[a]	10.1	0	0.35	0.035
347P-1	19.0	0	1.72	0.09
348P-1	22.7	0	0.94	0.04
349P-1	23.7	0	0.88	0.04
350P-1[a]	27.7	0	3.36	0.12
351P-1[a]	21.9	0	2.03	0.09
352P-1	15.1	0	0.60	0.04
353P-1	20.3	0	2.17	0.10

[a] These samples were ashed in Pyrex flasks.

Three red-cell samples were each split into two fractions. One fraction was ashed in a Pyrex flask; the other in a platinum dish. The difference in the manganese content of the fractions after ashing was so small that contamination from the Pyrex flasks could not be established. However, because a trace of manganese is present in Pyrex glass, platinum is recommended.

TABLE III

ANALYSIS OF HUMAN RED CELLS

Sample No.	*Sample weight g*	*Mn added μg*	*Mn found μg*	*Mn found p.p.m.*
345C-1[a]	5.1	0	1.23	0.24
347C-1	10.0	0	2.84	0.28
347C-2	10.1	0	3.00	0.30
348C-1[a]	8.8	0	3.92	0.45
348C-2	12.8	0	4.83	0.38
349C-1[a]	11.0	0	1.09	0.10
349C-2	12.6	0	1.22	0.10
350C-1[a]	10.1	0	2.87	0.28
350C-2	13.1	0	3.22	0.25
351C-1	11.8	8	11.20	—
351C-2	11.6	0	—	—
352C-1	5.8	8	8.40	—
352C-2	6.6	0	1.75	0.28
352C-3	5.1	0	0.91	0.18
353C-1	17.3	0	8.08	0.46

[a] These samples were ashed in Pyrex flasks.

TABLE IV

COMPOSITION OF SYNTHETIC RED-CELL ASH[a]

Metal ion	*Red-cell ash conc. p.p.m.*
Na	1200
K	400
Ca	20
Mg	60
Fe	500
Cu	0.9
Zn	12
Pb	0.6
Ni	0.06
Cr	0.02
Mn	(added separately to individual samples)

[a] Concentrations of the various metals were calculated either from ALBRITTON's values[5] or from those obtained spectrographically in the Pratt Trace Analysis Laboratory.

The results on human plasma and red cells are in good agreement with those given by ALBRITTON[5]: plasma, 0 to 0.25 p.p.m. and red cells, 0 to 0.48 p.p.m. with average values of about 0.1 and 0.2 p.p.m., respectively.

The accuracy of the method is shown by the results obtained with the synthetic samples and by the recovery of manganese added to split samples.

SUMMARY

A spectrophotometric method for the determination of manganese in human plasma and red cells with benzohydroxamic acid is presented. Interfering ions are removed by an anion exchange method, using Dowex-1, 8X resin. The manganese concentration found for plasma and red cells was about 0.1 and 0.2 p.p.m., respectively.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage du manganèse dans le plasma humain et dans l'hémoglobine, au moyen de l'acide benzohydroxamique. Les ions gènants sont éliminés par échangeurs d'ions. La teneur en manganèse trouvée est d'environ 0.1 p.p.m. dans le plasma et de 0.2 p.p.m. dans les globules rouges.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Mangan in menschlichem Blutplasma und roten Zellen mit Benzhydroxamsäure. Störende Ionen werden mit einem Austauscherharz entfernt. Es wurden im Plasma *ca.* 0.1 und in den roten Zellen *ca.* 0.2 p.p.m. Mangan gefunden.

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Anal. Chim. Acta, 26 (1962) 224–229

SPECTROPHOTOMETRIC DETERMINATION OF ALIPHATIC ALDEHYDE 2,4-DINITROPHENYLHYDRAZONES WITH 3-METHYL-2-BENZOTHIAZOLINONE HYDRAZONE

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INTRODUCTION

Hundreds of references are available in the literature on the detection, characterization, and determination of carbonyl compounds through their 2,4-dinitrophenylhydrazones[1–5]. The procedure for the trace analysis of these compounds usually has included the determination of their ultraviolet-visible absorption spectra in neutral and alkaline solutions. Another facet of this type of analysis has been examined only slightly[5] — the shift in the intensity and wavelength of the long-wave-length visible band with a change in the basicity of the solvent system[6].

In this paper is introduced an extremely sensitive procedure for the analysis of 2,4-dinitrophenylhydrazones of aldehydes. Other derivatives of aldehydes also can be analyzed; however, the analogous ketone derivatives do not react.

EXPERIMENTAL

Reagents

The 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) was purchased from the Aldrich Chemical Co., of Milwaukee, and was purified in our laboratory[7]. Its aqueous solution (0.3%) was stable for at least a week. All other hydrazones were prepared in our laboratory by standard procedures and were purified to a constant melting point by recrystallization. Purification of 2-methoxyethanol (hereafter called methyl cellosolve) was achieved by refluxing for 1 h in the presence of 0.1% MBTH and distilling over 0.2 g ferric chloride per 100 ml of liquid. After this treatment, the methyl cellosolve was placed in a brown bottle where it remained stable for at least 4 days.

Equipment

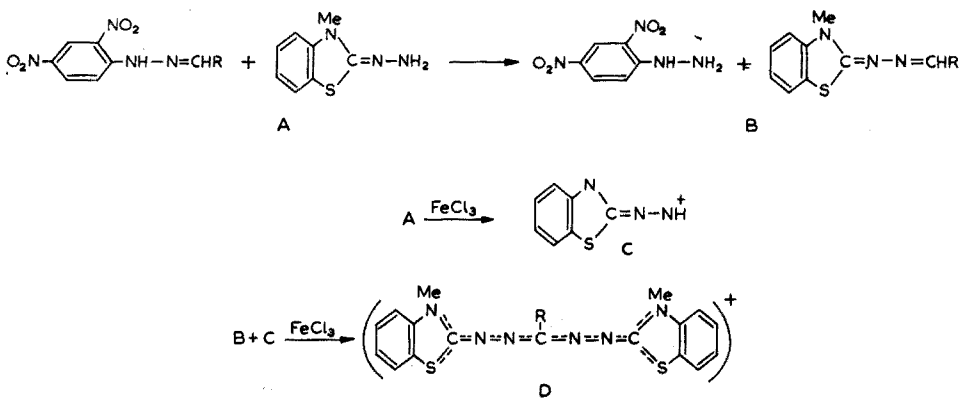
A Cary Model 11 Quartz Recording Spectrophotometer with 1-cm cells was used for all spectral determinations.

Spectrophotometric procedure

2 ml of the methyl cellosolve test solution was mixed with 2 ml of an aqueous 0.3% MBTH solution, and the mixture was allowed to stand at room temperature for 1 h. 2 ml of an aqueous 1% ferric chloride solution was added; the whole was allowed to stand another 3 min and then was diluted to 10 ml with methanol. The absorption spectrum was determined against the light-green blank.

MECHANISM OF THE REACTION

The reaction is postulated as taking place in the following fashion:



The reaction between B and C previously has been shown[7] to form the blue formazan cation, D, with the same spectral properties as those given in Fig. 1. In acetone the pure dye prepared from formaldehyde has a molar absorptivity of 76,000[8]. Consequently, if the aldehyde derivatives give a quantitative yield of the final chromogen in the analytical procedure, then the final molar absorptivity should be in the neighborhood of 76,000 for most of these derivatives.

DISCUSSION OF PROCEDURE

Variables in the procedure were determined. It should be noted that formaldehyde-2,4-dinitrophenylhydrazone was used as the standard in the development of this procedure and that this procedure then was applied to all other hydrazones tested.

The effect of the concentration of the reagent is shown in Fig. 2; greater concentrations than 0.4% produced a turbid solution. The concentration effect of the ferric chloride is shown in Fig. 3. In all observations, increasing the concentration of the reagent or the ferric chloride produced more color in the blank.

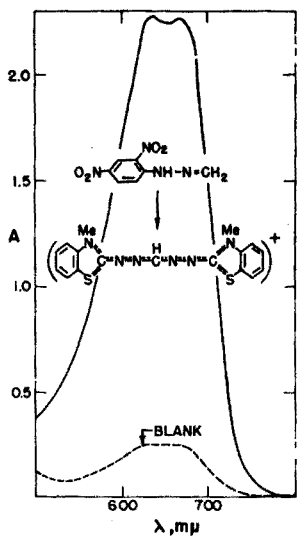


Fig. 1. Visible absorption spectra: Formaldehyde 2,4-dinitrophenylhydrazone reacted in the standard procedure. Final concentration $4 \cdot 10^{-5}$ *M* (———). Blank *versus* water (----).

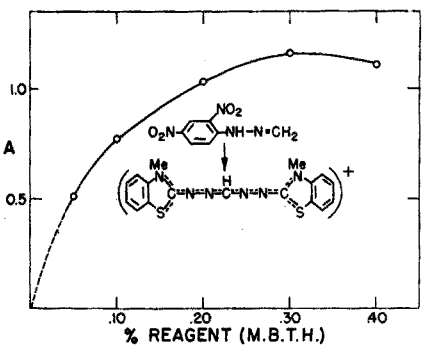


Fig. 2. Effect of concentration of 3-methyl-2-benzothiazolinone hydrazone on the absorbance obtained in the determination of formaldehyde 2,4-dinitrophenylhydrazone ($2 \cdot 10^{-5}$ *M*) at $\lambda_{max.}$ 673 mμ.

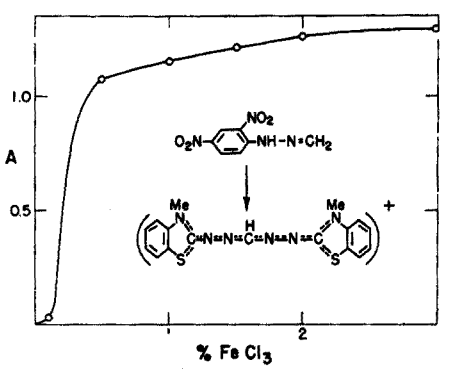


Fig. 3. Effect of concentration of ferric chloride on the absorbance obtained in the determination of formaldehyde 2,4-dinitrophenylhydrazone ($2 \cdot 10^{-5}$ *M*) at $\lambda_{max.}$ 673 mμ.

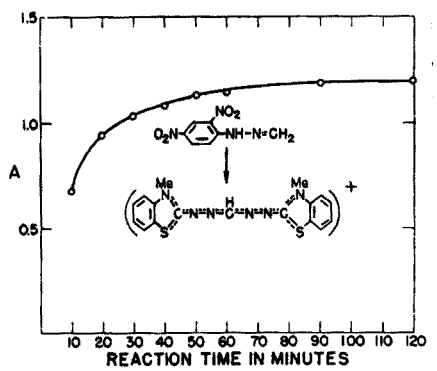


Fig. 4. Effect of reaction time between formaldehyde 2,4-dinitrophenylhydrazone ($2 \cdot 10^{-5}$ *M*) and 3-methyl-2-benzothiazolinone hydrazone on the absorbance obtained in the standard procedure.

A 60-min reaction time gave optimum absorbance. A longer reaction time produced no appreciable change, whereas a shorter reaction time gave a decreased absorbance (Fig. 4) in both sample and blank.

The effect of heating on a boiling water bath also was studied. The molar absorptivity increased rapidly when heating time was increased —maximum color development was observed after the reaction mixture was heated for 9 min at 100°. Longer periods of heating gave no appreciable change in absorbance, whereas a shorter heating time gave lower results. This heating procedure produced color in the blank four times as intense as that resulting from the standard procedure. Apparently heat in the presence of ferric chloride forms aldehyde.

At room temperature purified methyl cellosolve in a closed transparent container accumulates aldehydes at a fairly rapid rate; after exposure to daylight for several weeks, it gives a dark blue color in the reaction and an absorption spectrum closely similar to that obtained with aliphatic aldehydes. The procedure in which heating is used apparently forms aldehydes in larger amounts, as the more highly colored blank indicates. For best results the blank should have an absorbance less than 0.5 at the wavelength maxima, when it is compared to water. Other oxygenated solvents, such as ethanol, propanol, *t*-butanol, and *β*-chlorethanol, also apparently increased in

TABLE I

SPECTRAL DETERMINATION OF ALDEHYDE 2,4-DINITROPHENYLHYDRAZONES

Aldehyde	*Melting point* °C	$\varepsilon \cdot 10^{-3}$ *at* $\lambda_{max.}$	
		627s	*667*
Formaldehyde	166	57[a]	57
Acetaldehyde	168	71	77
Propanal	154	62	68
Butanal	122	58	64
2-Methylpropanal	187	33	36
Pentanal	98	54	60
2-Methylbutanal	125	39	44
Hexanal	104	53	59
Heptanal	107	53	58
Octanal	106	49	54
Nonanal	96	43	49
Decanal	104	25	30
Undecanal	104	22	24
Dodecanal	106	9	10
Acrolein	165	23	24
Crotonaldehyde	195	10.5	11

[a] $\lambda_{max.}$ is at 637 mμ.

aldehyde content just as quickly after distillation. Other solvents, such as dimethylformamide, N-methyl-pyrrolidone, acetone, acetic acid, and propionic acid gave poorer results than methyl cellosolve. An oxidation time of at least 3 min gave opti-

mum results. A shorter period gave lower absorbance readings; a longer period had no effect on the absorbance.

The final solution remained stable at an absorbance of 1.60 for 30 min but faded 0.03 absorbance units in 90 min. After standing 21 h the observed absorbance was 1.30. Beer's law was obeyed from 4 (absorbance = 0.10) to 85 μg per 10 ml of final solution. The absorptivity at 637 or 667 mμ was 0.27 μg^{-1} ml cm^{-1}.

The wavelength maxima and molar absorptivities obtained for all the compounds tested are recorded in Table I. All values in the table and those in the figures are based on a minimum of two determinations and are within $\pm 2\%$ of the average. The intensity value for formaldehyde 2,4-dinitrophenylhydrazone is based on 24 determinations and is 57,000 $\pm$ 1,000 at a wavelength maximum of 637 or 667 mμ.

INTERFERENCES

MBTH is a versatile analytical reagent and has been used to detect and determine trace amounts of the following compounds: aliphatic aldehydes[7]; aromatic primary amines, aralkylamines, aryldialkylamines, diarylamines, indoles, carbazoles, phenothiazines[9]; pyrroles, azo dyes, aminostilbenes, Schiff bases[10]; and *p*-hydroxystyrene compounds[11]. Consequently, all these compounds should be considered potential interfering compounds. Some appropriate step such as distillation or extraction with acid or alkali should remove most of these. In many cases, however, such interferences would not be present.

Aromatic aldehyde derivatives also can react, but the final colors are not as intense. For example, indole-3-aldehyde 2,4-dinitrophenylhydrazone, salicylalhydrazone, and benzaldehyde *p*-nitrophenylhydrazone give bands at 620 and 660 mμ with molar absorptivities of 15,000 or less. Aliphatic and aromatic ketone 2,4-dinitrophenylhydrazones give negative results in the test.

RESULTS

Aliphatic ketone and aldehyde 2,4-dinitrophenylhydrazones absorb at approximately 355 and 430 mμ in neutral and alkaline alcohol, respectively, with molar absorptivities of about 20,000 in both solvent systems[5]. Positive results in the MBTH procedure are obtained only with the aldehyde derivatives. Consequently, the aldehyde derivatives can be differentiated readily from ketone derivatives, which have similar absorption spectra in the same solvent. The resulting chromogens obtained from the aldehyde derivatives absorb at 667 mμ with molar absorptivities ranging around 60,000. With further improvement of this procedure a molar absorptivity of around 76,000 is possible. Thus, the procedure can at least triple the sensitivity usually attained in the determination of aliphatic aldehyde 2,4-dinitrophenylhydrazones.

The reactivity of the straight-chain aliphatic aldehyde 2,4-dinitrophenylhydrazones with MBTH in the procedure decreases, starting from the acetaldehyde derivative with each addition of a methylene group in the aldehyde moiety (Table I). The tetradecanal derivative forms a precipitate in the procedure.

Other aliphatic aldehyde derivatives also should be analyzable with the procedure. For example, heptanal oxime and heptanal thiosemicarbazole give molar absorptivities of 52,000 and 35,000 at the wavelength maximum of 667 mμ and 47,000 and 31,000 at the shoulder of 627 mμ, respectively.

SUMMARY

A sensitive new spectrophotometric procedure is described for the analysis of aliphatic aldehyde 2,4-dinitrophenylhydrazones. The chromogens formed in the procedure absorb at 667 mμ and are approximately three times as intense at this band as the starting aldehyde derivatives are in neutral and alkaline solvent at their wavelength maxima. With further improvement the procedure is capable of even greater sensitivity. Other aliphatic aldehyde derivatives also should be analyzable by this procedure, but 2,4-dinitrophenylhydrazones of ketones do not react.

RÉSUMÉ

Une nouvelle méthode spectrophotométrique très sensible est décrite pour le dosage de dinitro-2,4-phénylhydrazones d'aldéhydes aliphatiques, au moyen de méthyl-3-benzothiazolinone-2-hydrazone. D'autres dérivés d'aldéhydes aliphatiques pourraient également être analysés par ce procédé. Les dinitro-2-4-phénylhydrazones de cétones ne réagissent pas.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung aliphatischer Aldehyd-2,4-Dinitrophenylhydrazone mit 3-Methyl-2-Benzothiazolinonhydrazon. Die entsprechenden Ketoderivate geben keine Reaktion.

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SPECTROPHOTOMETRIC DETERMINATION OF URANIUM(VI) BY THE AZIDE REACTION

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The azide reaction has recently been used for the spectrophotometric determination of some transitional metal ions in solution. Ions such as copper(II)[1], cobalt(II)[2] and iron(III)[3] have been determined in this manner. Similarities between the azide and thiocyanate ions, both of which belong to the pseudohalide group, lead to the conclusion that the metal–azide linkage should show the same characteristics as that of the metal–thiocyanate. They have the same electronic structure[4], and they both give a red colour with iron(III). The yellow colour formed by uranyl ion with thiocyanate is similar to the colour produced with azide. The latter reaction has been examined for the spectrophotometric determination of uranium in aqueous media at a wavelength of 360 mμ[5]. However, a detailed study was not made.

In an initial study, we investigated the reaction of uranyl nitrate and sodium azide in aqueous solution[6]. The absorption spectrum of uranyl azide solutions was characterised by one well-defined peak with a maximum at a wavelength of 420 mμ. The possibility of the formation of different complex ions varying in the molar proportions of uranyl:azide from 1:1 to 1:3 was reported. With this possibility in mind we have studied more precisely the analytical application of this reaction to the spectrophotometric determination of uranium(VI) in solution.

Many methods are available for the determination of small amounts of uranium by means of liquid–liquid extraction, chromatographic separations, or electrolysis at the mercury cathode. A direct rapid colorimetric method which does not require such separations is obviously a distinct advantage. The method described here largely fills this need. Many of the transitional metal ions which might interfere by complexing the azide ion can be masked by EDTA. Furthermore, aqueous and aqueous acetone media containing uranyl azide are considerably more stable than the corresponding uranyl thiocyanate solutions usually employed. The proposed method has another advantage: it has a wide range of at least 5–180 p.p.m., hence it should be applicable for many purposes. The lower limit could be decreased further by the use of longer cells. This is especially promising as the absorbance of the reagent itself and of the uranyl salt is almost negligible at the wavelength of measurement. One limitation to the method is the need for a low hydrogen ion concentration, since an anion of a very weak and volatile acid is involved. However, the high sensitivity of the azide method makes it preferable, in our opinion, to thiocyanate methods, such as that

Anal. Chim. Acta, 26 (1962) 235–241

developed by CURRAH AND BEAMISH[7], where the major difficulties appear to be the poor colour stability, the dependence of colour intensity on the thiocyanate concentration over a wide range, and the interference from many anions.

EXPERIMENTAL

Uranyl nitrate hexahydrate and sodium azide (Merck grade) were used. A stock solution of about 0.1 *M* uranium was prepared and analysed gravimetrically by precipitation as ammonium diuranate and ignition to U_3O_8. The sodium azide solutions were analysed volumetrically by titration with a standard silver nitrate solution using potassium chromate as an indicator. A Unicam S.P.500 spectrophotometer, with 1-cm glass cells was used for colorimetric measurements. The pH-values were measured using a Cambridge portable pH meter, using a glass electrode and a calomel reference electrode. Other experimental techniques were described in a previous article[6].

RESULTS

Effect of reagents

Preliminary examination of the absorbance curves of uranyl azide solutions showed that the most practicable method of determining uranium directly was to make use of the good absorbance peak at 420 mμ. The absorbance of one series of solutions (total volume 25 ml) containing a fixed amount of uranyl (0.0008 *M*) and azide ions (0.32 *M*) and increasing amounts of nitric acid, was measured at 420 mμ. Maximum intensity was reached in a solution containing 0.06 *M* acid. Further increase in acid concentration resulted in a decrease in colour intensity. In another series of solutions the concentration of uranium was kept constant at 0.0008 *M*, the acid concentration was adjusted to that giving maximum intensity in the preceding experiment (0.06 *M*), and the azide concentration was varied from 0.32 to 0.96 *M*. Maximum intensity was obtained when the concentration of the azide was 0.8 *M*. The relative concentrations of the two reagents were therefore fixed at these levels.

TABLE I

CHANGES OF pH AND ABSORBANCY WITH ACID CONCENTRATION
Uranium, 0.0004 *M*; Azide, 0.8 *M*

ml of 0.1 M HNO_3	*Absorbance at 420 mμ*	*pH*
0	0.098	7.72
0.15	0.266	6.40
0.50	0.484	5.98
1.0	0.588	5.68
1.5	0.640	5.27
3.0	0.650	5.16
12.0	0.630	4.10

Effect of pH

The colour intensity of solutions containing uranyl azide was found to be very sensitive to changes in hydrogen ion concentration. In a series of solutions containing 0.0004 *M* uranium and 0.8 *M* azide, the pH was adjusted by the periodic addition of different amounts of nitric acid, keeping the total volume constant. The absorbances

and pH values were measured. The results are given in Table I. Within the pH range 4 to 7.7 the maximum colour intensity was obtained between 5 and 5.5. Regular buffer solutions could not be used to adjust the pH as the uranyl ion forms other interfering complexes (acetate buffer), or precipitates (phosphate buffers). At lower pH values, the weakly dissociated hydrazoic acid is formed and at higher pH basic uranyl azide precipitates. Subsequent measurements were therefore carried out in the pH range 5–5.5, which is concordant with the results obtained from the study of the effect of the reagents.

Effect of time, light and temperature

The reaction between uranium and excess of azide at the optimum hydrogen ion concentration proved to be instantaneous. The colour immediately developed fully and did not change in intensity for at least 48 h as long as the pH was maintained at 5–5.5. Measurements were therefore always carried out immediately after mixing. There was no significant difference between the absorbances of solutions kept in the dark and those exposed to daylight. The temperature however was found to affect the colour. When the absorbances were measured over the range 15–45°, an increase of 2% for every rise of 10° occurred. However, the absorbances were measured at room temperature, which was fairly constant through each series of measurement.

Conformity to Beer's law

For the verification of Beer's law, the absorbances at 420 mμ of uranyl azide solutions, containing different amounts of uranium but constant amounts of nitric acid (0.06 *M*) and sodium azide (0.8 *M*), were measured against a reagent blank. The results are shown in Fig. 1. This system obeys Beer's law within the range 2 and 180 p.p.m. of uranium. Two uranium solutions whose concentrations differed by only 1 p.p.m. could be differentiated at this wavelength. In an attempt to eliminate inter-

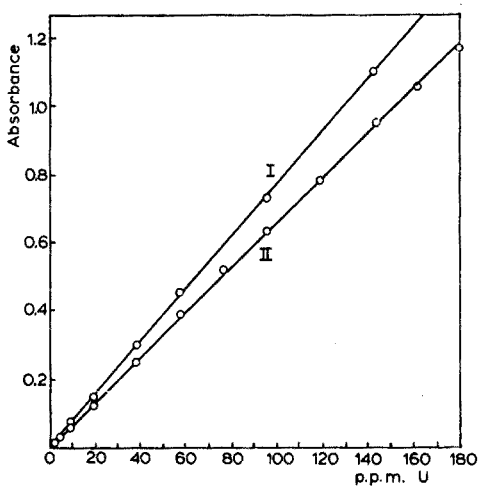

Fig. 1. Dependence of absorbance on uranium concentration at 420 mμ. N_3^- = 0.8 *M*; H^+ = 0.06 *M*. (I) in 70% v/v acetone, (II) in aqueous medium.

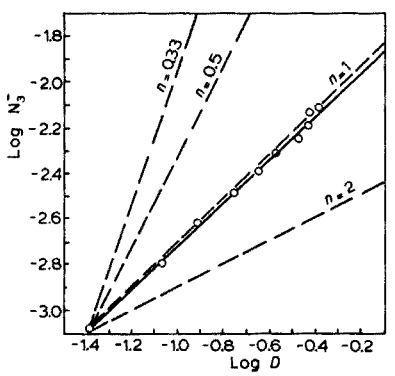

Fig. 2. Limiting logarithmic method at 420 mμ. UO_2^{+2} concentration is constant at 0.008 *M* and N_3^- concentration is varied. The circles are the experimental points. The dotted lines represent the theoretical values for n = 0.33, 0.5, 1 and 2 where n is the number of azide ions associated with the uranyl ion in the complex.

ferences and increase sensitivity, we investigated a system of lower dielectric constant in which the ionisation of most weakly acidic anions is greatly suppressed. A medium consisting of 70% v/v acetone in water was found satisfactory. Higher acetone ratios caused the precipitation of a gelatinous compound, probably basic uranyl azide. Beer's law was obeyed in this system over the same concentration range. When the absorbances were compared with those obtained using the thiocyanate as a reagent, it was found that the azide solutions were more intense in colour. The molar absorbance indices $\left(\frac{\text{absorbance}}{\text{cell length} \cdot \text{conc.}}\right)$ for a 0.00024 M solution of uranium and a cell length of 1 cm, were 1880, 1650 and 395 at 420 mμ for uranium azide in acetone, in water, and uranium thiocyanate in water respectively. Thus, in aqueous medium, the molar absorbance index for the azide is about four times larger than that for the thiocyanate. In acetone, the value for the azide is higher still. Measurements at 370 mμ showed that the azide is only twice as intense in colour as the thiocyanate: the absorbance indices are 4150 *vs.* 2000 for the same uranium concentration in aqueous solutions. At this wavelength, the azide colour in 70% acetone is also more intense than that in aqueous solutions.

Effect of different acids

Series of solutions containing 1 uranium : 2 azide molar ratio and increasing amounts of nitric, perchloric, sulphuric, hydrochloric or acetic acids were prepared and the total volume was kept constant. The absorbances of each series were measured at 420 mμ and compared with that of a solution containing the same uranium and azide concentration and no acid. Generally, increased acidity resulted in decrease in colour intensity. The effect of acid on the colour decreased in the order $CH_3.COOH > H_2SO_4 > HCl > HNO_3 > HClO_4$. These results are in agreement with the known complexing power of the respective anions. The acetate ion competes with the azide for a place in the coordination sphere whereas the perchlorate has least tendency to form complexes.

Effect of organic solvents

The colour of the uranyl azide solutions increased on the addition of miscible solvents such as acetone, ethyl alcohol, dioxane or isopropyl alcohol. In absence of the necessary amount of acid, precipitation occurred in solutions containing more than 70% by volume of the solvent. While the yellow thiocyanate complex of uranium can be extracted by certain immiscible solvents, the uranyl azide could not be similarly extracted. Solvents such as chloroform, carbon tetrachloride, ethyl acetate and ether were tried.

Interfering ions

In the evaluation of the precision of the method, 1 ml of 0.01 M uranium, 20 ml of 1 M sodium azide solution and 1.5 ml of 1 N nitric acid were diluted to 25 ml with water. The interfering ions were added to the original solution in the fashion of a spectrophotometric titration and the absorbances were corrected for dilution. The range of absorbances was about $\pm$0.005 absorbance unit from the average value obtained from 20 samples. A foreign substance was considered as interfering if the

absorbance of a solution containing 95 p.p.m. of uranium and the foreign substance had an absorbance 0.01 unit lower or higher than the average value for uranium azide alone. Iron(III) interfered seriously, but the addition of 1 ml of 0.2% EDTA solution reduced the interference appreciably and increased the maximum permissible amount of iron by about ten-fold. Excessive addition of EDTA is not recommended as some error is caused, probably owing to the participation of the EDTA in complex formation with the uranyl ion. Silver nitrate precipitated at once. Dihydrogen phosphate formed a precipitate after the addition of a few p.p.m. Thorium nitrate behaved similarly, but increased acidity prevented precipitation. However, the acid must not be so concentrated that the original colour is reduced through the displacement of the weakly dissociated hydrazoic acid. The results are given in Table II.

TABLE II

MAXIMUM TOLERANCE OF INTERFERING IONS

Concentration of uranium U = 95 p.p.m.; N_3^- = 0.8 *M*; H^+ = 0.06 *M*

Ion	*Added as*	*Maximum amount of ion tolerated, p.p.m.*
Fe^{+3}	$FeCl_3$	0.2
Fe^{+2}	$FeSO_4$	22
Cr^{+3}	$Cr(NO_3)_3$	41
Ni^{+2}	$NiCl_2$	17
Th^{+4}	$Th(NO_3)_4$	25 then ppt.
Ag^+	$AgNO_3$	ppt.
Ce^{+3}	$Ce(NO_3)_3$	280
Hg^{+2}	$HgCl_2$	560
Na^+	$NaNO_3$	370
Mn^{+2}	$MnCl_2$	110
$Cr_2O_7^{-2}$	$K_2Cr_2O_7$	34
$H_2PO_4^-$	$NH_4H_2PO_4$	14 then ppt.
WO_4^{-2}	Na_2WO_4	10
VO_3^-	NH_4VO_3	40
F^-	NaF	8

Structure of the complex

Our previous investigations[6] showed that the formation of a 1:1 uranyl azide complex, $UO_2N_3^+$, is possible. This assumption was further confirmed in the present work by applying the method of BENT AND FRENCH[8]. In one series of solutions the total concentration of uranium was kept constant at 0.008 *M* and that of azide was varied from 0.0008 to 0.0072 *M*, keeping the ionic strength constant at 0.032 by adding an appropriate amount of sodium perchlorate solution. The absorbance was measured at 420 mμ using a uranium solution as a blank. When the logarithms of the absorbance values were plotted against log N_3^- concentration, a straight line was obtained (Fig. 2). In another series of solutions the concentration of sodium azide was kept constant at 0.008 *M* and that of uranium was varied from 0.0008 to 0.0072 *M*,

keeping the ionic strength the same. When the logarithms of absorbance values were plotted against log UO_2^{+2} concentration, the curve shown in Fig. 3 was obtained. For the reaction

$$m\ UO_2^{+2} + n\ N_3^- = UO_{2m}N_{3n} \quad (1)$$

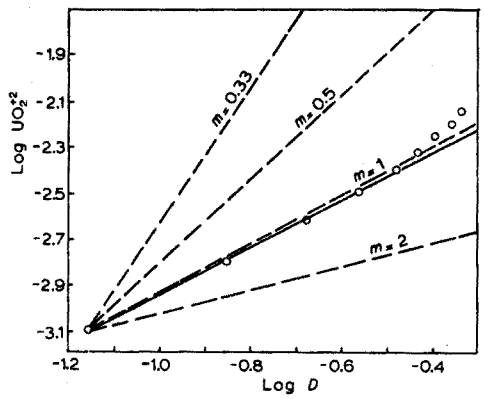

Fig. 3. Limiting logarithmic method at 420 mμ. N_3^- concentration is constant at 0.008 M and UO_2^{+2} concentration is varied. The circles are the experimental points. The dotted lines represent the theoretical values for m = 0.33, 0.5, 1 and 2 where m is the number of uranyl ions associated with the azide ion in the complex.

the absorbancy D will be proportional to the concentration of the coloured complex in the logarithmic expression

$$\log UO_{2m}N_{3n} = m \log UO_2^{+2} + n \log N_3^- + \log K \quad (2)$$

The experimental points agreed with the theoretical results, assuming the values of m and n to be one.

Determination of the instability constant

The molar ratio method of YOE AND JONES[9] was applied. For a constant uranium

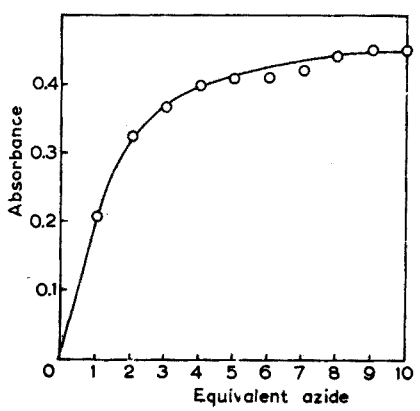

Fig. 4. Absorbance of uranyl azide solutions (UO_2^{+2} = 0.004 M) as a function of azide concentration (0–0.04 M) at 420 mμ.

concentration, a plot of the absorbance against increasing concentration of azide gave a smooth curve whose slope decreased gradually and became approximately parallel to the azide axis before again increasing in another smooth curve upon further addition of azide. The first part of the curve (Fig. 4) is assumed to represent the reaction leading to the formation of $UO_2N_3^+$. It is therefore possible to calculate the value of the instability constant, K, for reaction (1) assuming that a 1:1 complex is formed. The mean value for K under these conditions was found to be $2.3 \pm 0.27 \cdot 10^{-3}$.

SUMMARY

Azide has been investigated as a spectrophotometric reagent for uranium(VI). The system is more sensitive than the thiocyanate reaction. It obeys Beer's law in the range 2–180 p.p.m. of uranium. The colour is sensitive to hydrogen ion concentration; maximum absorbance and stability are attained at pH 5–5.5. Iron(III) interferes seriously, but can be masked by EDTA. Fe^{+2}, Cr^{+3}, Ni^{+2}, Th^{+4}, $Cr_2O_7^{-2}$, WO_4^{-2}, VO_3^- and F^- interfere. The deep yellow colour cannot be extracted with organic solvents. A mono-azido-uranium(VI) ion is present in dilute solutions; its dissociation constant is $2.3 \pm 0.27 \cdot 10^{-3}$.

RÉSUMÉ

L'azide est proposé comme réactif pour le dosage spectrophotométrique de l'uranium(VI). Cette réaction est plus sensible que celle obtenue avec le thiocyanate. L'influence des ions étrangers a été examinée.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Verwendung von Aziden als Reagenz bei der spektrophotometrischen Bestimmung von Uran-(VI). Die Reaktion mit Aziden ist empfindlicher als die Thiocyanatreaktion. Die störenden Kationen und Anionen werden angegeben.

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PHOTOMETRIC DETERMINATION OF ZINC IN METEORITES

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The zinc content of meteorites falls in a range (usually 1–100 p.p.m.) for convenient colorimetric determination with dithizone. The main problem lies in the separation of zinc from iron, nickel, and cobalt, especially from the latter two elements. The use of a strongly basic anion-exchange resin provides an easy solution to the separation problem. As shown by KRAUS AND MOORE[1], zinc is strongly adsorbed on Dowex 1 from 2 *N* hydrochloric acid, whereas cobalt and nickel are not appreciably retained. In 2.0 *N* hydrochloric acid the elution constants (distance in cm moved by the adsorption band maximum on elution with 1 ml of solution per cm^2 of resin column) have the following values: Fe(III)[2], 0.4; Cu(II), 1; Ni, 2.5 and Co, 2, so that elution with a moderate volume of hydrochloric acid of this concentration removes these metals from a column a few cm in length without loss of zinc (elution constant 0.0015). Zinc can then be eluted with 0.001 *N* hydrochloric acid, in which its elution constant is greater than 0.5.

A rough calculation indicates that a Dowex 1 resin column 3 cm long should safely hold zinc during elution of iron and other metals with 2 *N* hydrochloric acid. If the peak of the zinc band in the resin is assumed to have moved as much as 0.5 cm from the top of the column during the elution of iron and if the height equivalent to a theoretical plate (h) is as much as 0.5 cm, the zinc half-band width** in the resin is $\sqrt{2hl_{max}} = \sqrt{2 \cdot 0.5 \cdot 0.5} = 0.7$ cm. Accordingly, the peak of the zinc band lies 2.5/0.7 or 3.5 half-band widths from the base of the column, corresponding to a loss of $\sim 10^{-4}$ % of zinc, if the concentration in the adsorption band follows the normal distribution curve. A resin column of about 1 cm^2 cross sectional area should provide ample capacity.

The calculated amount of iron(III) remaining in a 3-cm resin column of 1 cm^2 cross section after elution with 50 ml of 2 *N* hydrochloric acid is $\sim 10^{-4}$ % (h again taken to be 0.5 cm, no doubt greater than the actual value for 100–200 mesh resin and moderate flow rate). If 0.5 g iron is present in the sample, this percentage corresponds to 0.5 μg Fe. If 25 ml of 2 *N* hydrochloric acid is used for elution, the calculated amount of iron remaining in the column is 0.1%, or 0.5 mg Fe with 0.5 g Fe in the sample. A qualitative experiment in which 200 mg of iron(III) was adsorbed on a 3-cm Dowex 1-X8 resin column of 0.8 cm^2 cross section showed that after elution with 40 ml of 2 *N* hydrochloric acid at a rate of 1 ml per min a trace of iron still remained, as

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** Defined as the distance between the sections in the column where the zinc concentrations are respectively the maximum and 1/e (= 0.37) of the maximum.

indicated by a very faint thiocyanate reaction on continued elution. The order of magnitude of the calculated value for elution of iron with 50 ml acid/cm^2 is thus verified. Actually, a sharp separation of zinc from iron is not required. The presence of as much as 0.5 mg of iron does not cause error in the determination of microgram amounts of zinc according to the recommended procedure below. Other elements of interest (especially Ni, Co and Cu) are eluted more easily than iron by 2 *N* hydrochloric acid so that they will be satisfactorily separated under the conditions eliminating most of the iron.

Elution of zinc is carried out with 0.001 *N* hydrochloric acid. This low chloride concentration assures retention of palladium(II) on the resin, while permitting quantitative elution of zinc with less than 25 ml of solution.

After separation, zinc is determined by the familiar dithizone method[3] in which thiosulfate is used as a complexing agent in acetate solution for the few foreign elements not separated by ion-exchange. Alternatively, the method in which diethanoldithiocarbamate is used as a complexer can be applied[4]. Cadmium accompanies zinc quantitatively in the ion-exchange separation but is not likely to cause error, even if not complexed, because the ratio Zn/Cd is probably greater than 100. Actually thiosulfate complexes cadmium satisfactorily in amounts likely to be encountered in meteorites.

Silicate meteorites are decomposed with hydrofluoric and sulfuric acids. Sulfuric acid has been used in place of perchloric acid to assure the complete expulsion of fluoride. Calcium sulfate formed in the decomposition of 1-g samples of chondrites

TABLE I

DETERMINATION OF ZINC AFTER ION-EXCHANGE SEPARATION

Addition	*Zn taken* μg	*Zn found* μg
200 mg Fe(III), 50 mg Ni, 5 mg Co	1.00	0.99
	2.00	2.12, 1.89
	4.00	3.76
	10.0	10.0
200 mg Fe(III), 50 mg Ni, 5 mg Co, 5 μg Cd	10.0	10.0
1.2 mg Mn, 120 μg Cu, 12 μg Sn, 6 μg Pb;	1.00	1.03
2 μg each of Ru, Rh, Ir, Pt, Ag, Au, Cd, Hg, In, Tl, Sb, Te	4.00	3.97
10 μg Pd	4.00	3.90
200 mg Fe(III), 150 mg Mg, 50 mg Ca, 25 mg Al[a]	2.00	2.17
	4.00	3.74, 3.76
	10.0	9.3
400 mg Fe(III), 300 mg Mg, 100 mg Ca, 50 mg Al[a]	100	96, 96
0.6 g iron meteorite[b]	25.0	23.8

[a] Solution evaporated with sulfuric and hydrofluoric acids as in analysis of silicate meteorites.
[b] 25 μg zinc added to a solution of 0.6 g of Henbury iron which had been passed through resin column to remove original zinc.

can be brought into solution with the 50 ml of 2 *N* hydrochloric acid called for in the procedure. The presence of the sulfate does not interfere in the ion-exchange separation of zinc. Possibly perchloric acid can be used in place of sulfuric acid, and, if so, would be preferable in the decomposition of high-calcium achondrites.

Small amounts of platinum (and other platinum metals) derived from the platinum ware and the meteorites themselves form an orange-brown zone at the top of the resin column, but are not eluted with zinc.

Results obtained in applying the proposed method to samples simulating iron and silicate meteorites are given in Table I. Blanks were run to correct for zinc in the mixtures. The average deviation from the true value in 16 determinations (1–100 μg Zn) is 4%. The largest deviation is 8.5%; 3 results are high and 11 are low, showing a tendency toward low values, which is the normal behavior in trace analyses involving separations and more or less complex manipulations.

When the proposed method was applied to meteorites the unpleasant discovery was made that reproducible results were often not obtained when ~1-g samples of irons and chondrites were taken. This behavior is illustrated in Table II. The Canyon Diablo iron gave zinc values ranging from 32 to 42 p.p.m. in 7 samples. Aliquots of the same sample solution gave values agreeing within 1–2% (*e.g.* 39.0 and 39.2, 32.4

TABLE II

REPLICATE DETERMINATIONS OF ZINC IN IRONS AND CHONDRITES

Meteorite	*Sample* g	*Zn* p.p.m.
Canyon Diablo	0.2	32
	0.65	42
	0.65	35
	0.65	38
	1.25	39.0, 39.2[a]
	2.5	32.4, 32.0[a]
	2.5	41.0, 41.4[a]
Henbury	0.6	27
	0.6	38
	1.25	31.7, 32.2[a]
Plainview (chondrite)	0.6[b]	42.3
	0.6[b]	41.9
	1.0	62
	1.0	41
	1.1	72
Holbrook (chondrite)	1.2	42
	0.9	35
Richardton (chondrite)	1.1[b]	65
	1.1[b]	66
	0.7	64

[a] Values from aliquots of the same solution
[b] Samples of the same powder

and 32.0 p.p.m.), so that the greater part of these variations must be attributed to a non-uniform distribution of zinc. Other irons show the same behavior in greater or less degree. The variability in zinc distribution is believed to be due largely to the varying FeS content of the samples. It is known that troilite in irons has, or may have, a high zinc content (~1000 p.p.m.).

Chondrite samples of ~ 1-g size can also show strongly variable zinc contents. This is brought out by analysis of the polymict chondrite Plainview. Four samples of approximately 1 g weight gave values ranging from 41 to 72 p.p.m. (Table II). Less heterogeneous chondrites can still give perceptible differences on a 1-g scale (Holbrook). Again non-uniformity in the distribution of troilite accounts for the variable zinc contents. On the other hand, some chondrites (such as Richardton) seem to have a fairly uniform distribution of zinc, if agreement of results on two samples of 0.7 and 1.0 g weight can be taken as a criterion.

At this time it is impossible to state what weight of an iron should be taken on the average to yield a moderately accurate mean value for zinc. No doubt the sample size required will vary from one iron to another. The sampling problem becomes formidable when large inclusions of troilite must be taken into account. For determination of zinc in the iron phase small samples may suffice if they can be finely divided and some method devised for removing troilite, or applying a correction for the zinc it contributes. When a sufficient amount of chondrite is available, a fairly representative sample can usually be obtained by crushing a requisite amount of material.

The procedure below calls for the use of a 1-g sample of meteorite, the selection of which depends upon the specimen and the end in view.

The following values are typical of reagent blanks, carried through the entire

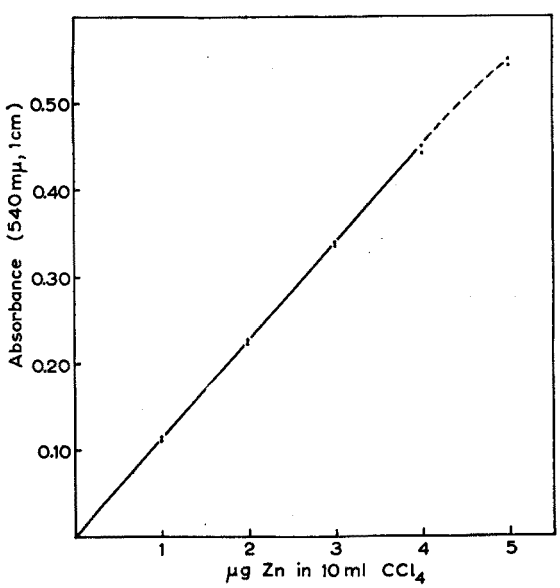

Fig. 1. Standard curve for the determination of zinc with dithizone. Absorbance for 0 μg Zn (= 0.32) has been subtracted. The two points for each zinc concentration represent readings with two different dithizone solutions at a time interval of 3 months.

procedure, for silicate meteorites: 0.25, 1.0, 0.75 and 0.5 p.p.m. Zn (from 1/25 aliquot ≡ 40 mg sample); 0.4, 1.5, 0.6 and 1.0 p.p.m. Zn (2/25 aliquot ≡ 80 mg sample). The variation is not much greater than the photometric error. The average blank value is a little less than 1 p.p.m. Zn. Since the zinc content of chondrites usually falls in the range 25–70 p.p.m., a blank of this magnitude is of little importance for them. Achondrites may contain only a few p.p.m. of zinc and here the blank is important. The reagent blank for irons was found to amount to 0.8 ± 0.5 p.p.m. Zn. The zinc content of some irons may be as low as 2–3 p.p.m., so that the zinc blank is important in such cases.

A typical standard curve for the dithizone mixed-color procedure is reproduced in Fig. 1 to show the reproducibility and sensitivity. A linear relation between zinc concentration and absorbance holds up to 4 μg Zn in 10 ml of carbon tetrachloride.

EXPERIMENTAL

Resin column

Use a 5–6-cm tube of 1.0 cm diameter, fitted with a stopcock, to hold the resin. Place a thin layer of glass wool above the stopcock. Add a slurry of Dowex 1-X8 resin, 100–200 mesh, to form a column 3 cm in length. Cover with a little glass wool.

Special solutions

Water, redistilled. Alternatively, zinc can be removed with ion-exchange resin.

Hydrochloric acid, about 6 *N*. Distil 1 : 1 hydrochloric acid in Pyrex. *Hydrochloric acid*, 2.0 *N*. Pass 2.0 *N* hydrochloric acid through a column of Dowex 1-X8 resin to remove zinc. *Hydrochloric acid*, 0.001 *N*.

Ammonium hydroxide, 4 *N*. Pass ammonia gas from a cylinder into pure water, and dilute to make the ammonia concentration approximately 4 *N*. Store in a polyethylene bottle.

Dithizone, 0.0010% (w/v) solution in pure carbon tetrachloride, prepared from dithizone of adequate purity. The solution is best prepared every 10 days by dilution of 0.01% carbon tetrachloride stock solution. Keep these solutions in a refrigerator.

Acetate buffer, pH 4.75. Mix equal volumes of 2 *M* sodium acetate and 2 *N* acetic acid. Remove reacting heavy metals by shaking with successive portions of 0.01% dithizone in carbon tetrachloride. Filter the aqueous solution through a small filter paper to remove droplets of carbon tetrachloride.

Sodium thiosulfate, 25 g of $Na_2S_2O_3 \cdot 5\ H_2O$ in 100 ml of water.

Standard zinc solution, 100 μg Zn per ml of 0.1 *N* hydrochloric acid. Dissolve reagent-grade 20- or 30-mesh zinc in a slight excess of hydrochloric acid and dilute to volume. From this solution prepare by dilution with redistilled water a solution containing 1.00 μg Zn per ml of 0.01 *N* hydrochloric acid.

Procedure

Decomposition of iron meteorites. Dissolve 1 g of sample (see discussion above) in a mixture of 20 ml of 6 *N* hydrochloric acid and 3 ml of concentrated nitric acid. Evaporate the solution to near dryness. Add 10 ml of 6 *N* hydrochloric acid and evaporate almost to dryness to destroy nitric acid. Repeat the evaporation with another 2-ml portion of hydrochloric acid, and take up the residue with 20 ml of 2 *N* hydro-

chloric acid. Collect any insoluble material on a small filter paper and wash with 2 *N* hydrochloric acid. Ignite the paper and contents in a small platinum crucible and fuse the residue with 0.5 g of sodium carbonate. Take up the melt in 2–3 ml of water and add 3 ml of 6 *N* hydrochloric acid. Combine the solution with the main portion in a 50-ml volumetric flask and make up to the mark with 2 *N* hydrochloric acid.

Decomposition of silicate meteorites. Treat 1 g of powdered sample with 3 ml of water and 3 ml of 1 : 1 (9 *M*) sulfuric acid in a platinum dish, and heat gently on a hot plate. After about 20 min, when sulfide has been decomposed, add 5 ml of hydrofluoric acid, and heat at gradually increasing temperature with occasional stirring until most of the excess sulfuric acid has been expelled. Cool, add a few ml of water, 0.5 ml of concentrated nitric acid, and 1 ml of 1 : 1 sulfuric acid and again expel most of the sulfuric acid. Take up the residue in 20 ml of 2 *N* hydrochloric acid. Warm, filter off insoluble material on a small filter paper and wash with a little 2 *N* hydrochloric acid. Burn the paper in a platinum crucible, fuse the residue with 0.5 g of sodium carbonate, take up the melt in 2–3 ml of water, add 3 ml of 6 *N* hydrochloric acid, and warm. Combine the solution with the main portion in a 50-ml volumetric flask and dilute to the mark with 2 *N* hydrochloric acid.

Separation of zinc. Wash the resin column with 20 ml of 1 *N* nitric acid and then with 10 ml of 2 *N* hydrochloric acid. Pass 20.0 ml of the iron meteorite sample solution or 10.0 ml of the silicate meteorite sample solution through the column at a rate of 0.5–0.6 ml/min. Wash the column with 30 ml of 2.0 *N* hydrochloric acid at the same rate and discard this solution. Elute zinc by passing 25 ml of 0.001 *N* hydrochloric acid through the column at the same flow rate into a 25-ml volumetric flask. Adjust to the mark and mix.

Determination of zinc. Transfer an aliquot of the 0.001 *N* hydrochloric acid eluate containing ~ 0.3 to 4 μg Zn (usually 5–10 ml) to a separatory funnel, and dilute to 10 ml with water. Neutralize the solution to thymol blue with a few drops of 4 *N* ammonium hydroxide (color change from red to yellow). Add 5.0 ml of acetate buffer and 1.00 ml of sodium thiosulfate. Shake vigorously for 2 min with 10.0 ml of 0.0010% dithizone in carbon tetrachloride. Dry the stem of the funnel with filter paper, and run the carbon tetrachloride extract into a 1-cm cell through a small plug of glass wool in the stem. (The glass wool should be purified by washing with dilute nitric acid, dithizone solution, and carbon tetrachloride).

Measure the absorbance at 540 mμ against carbon tetrachloride in the reference cell. Subtract the blank obtained by the same procedure. Construct the standard curve by taking 0, 1, 2, 3, 4, 5 μg of zinc, and treating as described above, beginning with *Determination of zinc.*

ACKNOWLEDGEMENT

We are indebted to the National Science Foundation for the post-doctoral grant that made this study possible.

SUMMARY

Zinc is determined in iron and silicate meteorites by the spectrophotometric dithizone method after separation from iron(III), nickel, cobalt, copper and other elements by ion exchange on Dowex 1-X8 resin in hydrochloric acid solution. The distribution of zinc is so heterogeneous in some irons and chondrites that 1-g samples do not give reproducible values.

RÉSUMÉ

Le zinc, dans les météorites ferreux et silicatés, est dosé spectrophotométriquement par la dithizone après séparation du fer(III), du nickel, du cobalt, du cuivre, etc. par échangeur d'ions. Dans certains cas, la répartition du zinc dans l'échantillon à analyser est tellement hétérogène que des prises d'un gramme ne donnent pas des résultats reproductibles.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Zink in Eisen- und Silikatmeteoriten mit Dithizon. Eisen-(III), Nickel, Kobalt, Kupfer und andere Elemente werden vorher mit einem Austauscherharz entfernt. Wegen der ungleichmässigen Verteilung des Zinks konnten in einigen Fällen bei 1 g Einwagen keine reproduzierbaren Werte erhalten werden.

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MICRODOSAGE COLORIMÉTRIQUE DE LA CYSTÉÏNE ET DE LA CYSTINE

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Nous avons été amenés à étudier une méthode de dosage de la cystéïne et de la cystine qui permette son emploi en milieu biologique. Elle a comme caractères d'aboutir à une réaction colorée se prêtant à un dosage photométrique dans le spectre visible; d'être facile à mettre en oeuvre, et de posséder une bonne sensibilité. Nous ne décrirons ici que la technique utilisée pour le dosage en solutions pures.

PRINCIPE

La thiofluorescéïne (TF) est un réactif que nous avons déjà utilisé pour le dosage des peroxydes lipidiques[1,2] car elle a la propriété d'être bleue en solution alcaline et de se décolorer sous l'influence d'un agent oxydant tel que l'iode. On obtient le même effet par l'oxygène moléculaire sous l'action d'une forte lumière.

Cette décoloration traduit très probablement l'oxydation des groupes —SH de la

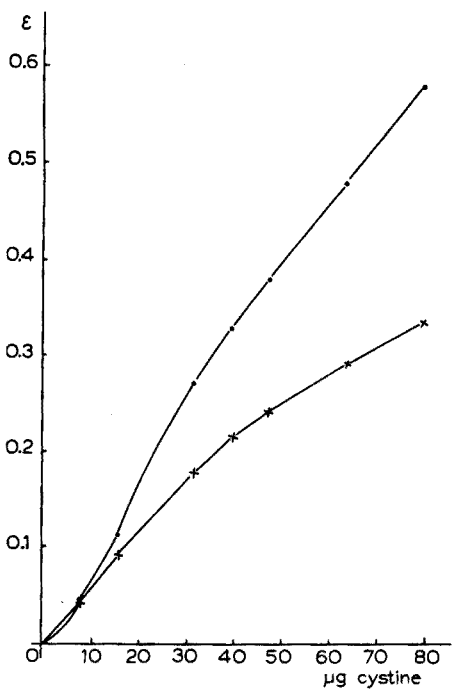

Fig. 1. ● Points obtenus avec une solution de TF ayant, avant décoloration, une densité optique de 5. × Points obtenus avec une solution de TF ayant, avant décoloration, une densité optique 3. λ = 5850 Å; l = 2 cm.

molécule de TF. En milieu acide, deux atomes d'iode décolorent quantitativement une molécule de pigment.

Dans certaines conditions, cette réaction est réversible sous l'action d'un excès de groupes —SH. Ce phénomène est certainement complexe. Nous nous contenterons de préciser les points suivants, sans proposer les diverses hypothèses qui peuvent les expliquer.

(*a*) Seule la décoloration par la lumière donne un composé qui se recolore sous l'action des groupes —SH.

(*b*) Tous les porteurs de groupes —SH que nous avons essayés sont actifs; SH_2 en milieu alcalin, cystéïne, glutathion, cystéamine, SH protéïques. Mais la courbe spectrale du composé coloré n'est pas exactement identique à celle de la TF; elle varie quelque peu, soit avec le corps réducteur, soit avec la température à laquelle se produit la réaction.

(*c*) Il s'agit d'une réaction équilibrée, et incomplète s'il n'y a pas un très gros excès de groupes réducteurs. La courbe exprimant la concentration de la forme colorée, en fonction de la quantité de substance réductrice, est complexe (Fig. 1), Elle présente à son origine une inflexion qui oblige à adapter les quantités de réactif à l'ordre de grandeur présumé de la cystéïne à doser*.

Le principe de la technique est donc le suivant: On décolore par la lumière une solution alcaline de TF. On introduit le corps à doser. On accélère la réduction par un chauffage convenable, et on mesure la coloration obtenue à 5850 Å.

TECHNIQUE

Préparation de la thiofluorescéïne

Nous l'avons indiquée précédemment[1]: on traite le chlorure de fluorescéïne par NaSH en solution alcoolique. Quelques modifications rendent cette préparation plus aisée.

Le chlorure de fluorescéïne est actuellement un produit commercial**. Il est nécessaire de le purifier en le lavant, en colonne, par de la potasse alcoolique, et de le recristalliser dans le chloroforme. Le chlorure, une fois purifié, doit être à peine coloré.

A 1 g de dichlorure de fluorescéïne on ajoute une solution de NaSH obtenue en faisant barbotter pendant 3 h du SH_2 dans 100 ml d'éthanol où l'on a dissous 1 g de sodium.

On fait bouillir à reflux pendant 30 min. La solution devient d'un bleu intense. Après refroidissement on neutralise par CH_3COOH. Le précipité formé est filtré rapidement au Büchner puis séché par broyage avec 50 à 100 fois son volume de Na_2SO_4 anhydre.

On extrait en colonne par CS_2 pur jusqu'à ce qu'une goutte d'éluat, évaporée sur un morceau de papier filtre, ne donne plus qu'une coloration bleue très faible par exposition à des vapeurs d'ammoniaque. On ajoute égal volume d'éther de pétrole et on distille au bain marie jusqu'à moitié environ du volume initial. On filtre pour éliminer un précipité blanc floconneux. On abandonne une nuit au réfrigérateur. On

* Il est possible que cet accident soit du à une impureté de la TF. Cependant plusieurs préparations de ce produit, parfaitement cristallisées, ont donné exactement la même courbe.

** Nous avons utilisé le produit livré par la firme B.D.H.

recueille les cristaux jaunes pâles qui, séchés, sont conservés dans de petits tubes sous vide.

Préparation des réactifs

(*a*) *Solution de thiofluorescéïne.* On réalise une solution de thiofluorescéïne dans l'acétate d'éthyle à environ 2 mg/ml. Cette solution doit être conservée à la glacière. A une certaine quantité de tampon phosphate pH 8, 0.1 *M*, on ajoute une quantité de solution de TF telle qu'après dilution au 1/5 elle présente une absorption convenable et dont nous préciserons plus loin la valeur. Puis on décolore cette solution par exposition à la lumière d'une lampe de 100 W à 15 cm. (Durée 15 min environ).

(*b*) *Solution de borate de sodium,* 0.2 *M.*

(*c*) *Solution d'acide borique et de KCl,* l'un et l'autre 0.2 *M.*

(*d*) *Solution cyanurée.* On fait une solution avec: KCN 130 mg, et solution borique ci-dessus: 10 ml.

(*e*) *Solution de cystine* à 0.800 mg/ml qui servira d'étalon. La cystine est dissoute dans quelques gouttes d'HCl environ 4 *N.* On complète par de l'eau distillée. La solution est stable.

Conduite du dosage

(*a*) *Dosage des SH (cysteïne).* Dans un tube à essai on introduit successivement: 1.2 ml de la solution d'acide borique, 1.2 ml de borate de Na, 1 ml de la solution à doser, contenant entre 0.01 et 2 μmoles, et 5 ml de solution de thiofluorescéïne décolorée.

Comme nous l'avons dit, la courbe d'étalonnage présente une inflexion à l'origine, qui rend incertaines les mesures portant sur de très faibles quantités de cystéïne (inférieures à 5 μg). On rend cette inflexion négligeable en opérant avec une solution de TF peu concentrée. Il y a avantage au contraire à utiliser une solution concentrée si les quantités présumées de cystéïne sont supérieures.

Dans le premier cas (très faibles concentrations) on utilisera une solution de TF qui, avant décoloration, aura une densité optique, mesurée à 5900 Å, sous 1 cm, après dilution au 1/5, de l'ordre de 0.5 à 0.6. Dans le second cas on adoptera un réactif ayant une densité optique deux à trois fois plus forte.

Nous utilisons comme témoin une solution de cystine, qui est parfaitement stable: on la traite par KCN pour la transformer, molécule à molécule, en cystéïne, selon le mode opératoire indiqué ci-après. On dressera, pour chaque dosage, une courbe d'étalonnage avec 4 à 5 témoins à des concentrations convenables.

La recoloration est lente. On peut selon le liquide à étudier, soit abandonner la réaction à elle même pendant 15 h au réfrigérateur à 4°; soit chauffer 30 min au bain marie à 50°; soit opérer à 70° pendant 4 min.

Au bout de ce temps on refroidit, ou on réchauffe, les tubes en les plaçant pendant 15 min dans l'eau à la température du laboratoire. La lecture est faite ensuite au spectrophotomètre. Bien que la courbe ait un maximum très arrondi, nous prenons habituellement trois points: 5800, 5850 et 5900 Å. Un photomètre à filtre donnerait probablement des résultats satisfaisants en raison précisément de la grande largeur de la bande. Il y a avantage, surtout pour les faibles quantités de cystéïne, à opérer dans une cuve de 2 cm d'épaisseur.

Le coefficient d'extinction spécifique varie un peu avec la préparation de TF, et a

tendance à diminuer lorsqu'elle vieillit: c'est pourquoi un étalon est nécessaire. Les densités optiques par 0.1 μmole de cystéïne (soit 12.1 μg) sous 2 cm, sont de l'ordre de 0.15.

(*b*) *Dosages des SS (cystine).* Dans un tube à essai on introduit: 1.2 ml de solution d'acide borique, 0.4 ml de solution de borate de sodium, 0.8 ml de solution cyanurée, 1 ml de solution à doser contenant entre 0.01 et 2 μmoles de SS. Dans un second tube on introduit les mêmes réactifs, mais on remplace la solution de cystine par 1 ml d'eau. Ce témoin est nécessaire, car KCN provoque une légère coloration de la TF oxydée. On laisse 10 min à la température du laboratoire puis on dose comme ci-dessus.

Bien entendu après action de KCN, un groupe SS est dosé comme un seul groupe SH.

Plusieurs centaines de dosages effectués avec cette méthode ont montré sa grande sensibilité. Son utilisation en milieu biologique, qui n'a pas été décrite ici, montre néanmoins qu'elle n'est influencée, ni dans un sens ni dans l'autre, par d'autres acides aminés ou par les dérivés oxygénés de la cystéïne. La méthode paraît donc assez spécifique des groupes SH et SS. Les réactifs, à l'exception de la solution de KCN qui doit être renouvelée journellement, se conservent bien. Elle est donc d'un maniement aisé et rapide. Nous en avons précisé la technique dans le cas de la cystéïne et de la cystine. Mais il est vraisemblable qu'elle pourrait être sans difficulté étendue aux autres molécules possédant des groupements sulphydryles.

RÉSUMÉ

La thiofluorescéïne décolorée par la lumière en milieu alcalin, se recolore sous l'action des groupes —SH. On peut par ce moyen doser colorimétriquement des quantités de cystéïne et de cystine de l'ordre du dixième de μmole.

SUMMARY

Thiofluorescein is bleached in alkaline medium by light but reforms its colour on reaction with —SH groups. This can be used for the colorimetric determination of cystine and cysteine in the micromolar range.

ZUSAMMENFASSUNG

Thiofluorescein wird in alkalischer Lösung durch Lichteinwirkung entfärbt. Durch HS-Gruppen wird wieder Farbbildung verursacht. Diese Eigenschaft der HS-Gruppen wird zur Bestimmung von mikromolaren Mengen Cystin und Cystein angewandt.

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THE DETERMINATION OF SOME ALIPHATIC ALCOHOLS AND ALDEHYDES BY OXIDATION WITH ACID POTASSIUM DICHROMATE

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The oxidation of primary aliphatic alcohols is customarily represented by the equations

$$RCH_2OH + O = RCHO + H_2O; \quad RCHO + O = RCOOH$$

and these form the basis of an analytical method for the determination of methanol and ethanol[1]. The method is simple to perform and has the advantage of not requiring any of the specialised apparatus needed by more sophisticated techniques, *e.g.* gas chromatography. However, with higher alcohols the reactions no longer follow these equations precisely[2] and it was with the aim of elucidating the nature of the processes then occurring that this investigation was concerned.

The mechanisms of oxidation by compounds of chromium have recently been reviewed by WATERS[3]. The overall reduction of dichromate to chromium(III) undoubtedly proceeds by a series of simple stages, probably each involving only one or at most two electron transfers and in acid solution the active oxidising species has been shown by WESTHEIMER AND NOVICK[4] to be $(HCrO_4)^-$.

The oxidation of alcohols is thought to proceed via a rapid reversible acid-catalysed esterification to the chromate ester followed by a slower oxidation[5]. On the other hand the oxidation of aldehydes is generally believed to proceed via the tautomeric enol form; for example, in the oxidation of propionaldehyde and butyraldehyde by manganic pyrophosphate[6], the first detectable oxidation products are the α-hydroxyaldehydes.

The occurrence of carbon–carbon bond cleavage has been reported in oxidation of various alcohols and aldehydes. For example, CONANT AND ASTON[7] reported that acetone was formed in the oxidation of isobutyraldehyde with dilute acid dichromate at 80°, and DRUMMOND AND WATERS[8] found that in the oxidation of aldehydes and ketones with alkaline permanganate and with acid manganic salts, stepwise degradation of the hydrocarbon chain occurred probably via the enolic anions. More recently JONES AND WATERS[9] have demonstrated that carbon–carbon bond fission occurs in certain oxidations with V^{+6}, but in no case has there been a detailed study of the products of the reaction.

EXPERIMENTAL AND RESULTS

The purest commercially available reagents were used.

Stoichiometry

The amounts of oxygen consumed by known weights of ethanol, *n*-propanol, isopropanol and *n*-butanol were determined as follows. A known weight of the alcohol was introduced into a 250-ml pressure bottle and an excess of standard 0.1 *N* potassium dichromate solution was added followed by 50 ml of 2 *N* sulphuric acid. The stoppered bottle was then heated in a boiling water bath for at least 1 h, trial experiments having shown that this was the time required for complete reaction, except in the case of isopropanol for which 30 min heating sufficed. Further heating caused no increase in the amount of dichromate consumed. At the completion of the heating, the bottle and its contents were cooled and the unused dichromate was reduced by a measured excess of standard ferrous ammonium sulphate. The unoxidised ferrous ammonium sulphate was then titrated against the standard dichromate using barium diphenylamine sulphonate indicator and thus the volume of dichromate consumed by the alcohol was obtained. Some typical results are presented in Table I, where it is shown that the experiments with isopropanol confirmed entirely WESTHEIMER's conclusion that the oxidation of this alcohol to acetone is essentially quantitative[5]. The values of *n* recorded in Table I were independent of concentration of sulphuric acid in the range 3 to 10% (v/v).

Similar experiments were also carried out using propionaldehyde and *n*-butyraldehyde. Both series of experiments were performed over wide ranges of concentration of organic substrate and dichromate, and these results are summarised in Table II.

TABLE I

OXIDATION OF SOME ALCOHOLS WITH ACID 0.1 *N* POTASSIUM DICHROMATE

(g = wt. alcohol taken, *n* = number of atoms oxygen absorbed by one mole of alcohol)

ethanol		*n-propanol*		*isopropanol*		*n-butanol*	
g	*n*	*g*	*n*	*g*	*n*	*g*	*n*
0.0017	1.94	0.0060	2.76	0.0105	1.03	0.0080	2.88
0.0041	1.99	0.0100	2.77	0.0310	1.02	0.0093	3.02
0.0216	1.99	0.0139	2.75	0.0419	0.97	0.0124	3.00
0.0235	1.97	0.0199	2.79	0.0502	1.00	0.0203	2.98
0.0425	1.95	0.0376	2.82	0.0523	1.00	0.0318	3.02
	Mean 1.97		Mean 2.78		Mean 1.00		Mean 2.95

TABLE II

EFFECT OF STRENGTH OF ACID POTASSIUM DICHROMATE SOLUTION ON OXIDATION OF ALCOHOLS AND ALDEHYDES

$K_2Cr_2O_7$ *N*	*Number of atoms of oxygen absorbed in oxidation by one mole of*			
	n-propanol	*propionaldehyde*	*n-butanol*	*n-butyraldehyde*
0.1	2.78	1.69	2.95	1.93
0.2	2.78	1.72	2.92	1.92
0.5		1.70	2.93	1.91
1.0	2.82	1.72	2.93	1.92

Product analyses

The organic products of the oxidations of *n*-propanol, propionaldehyde, *n*-butanol and *n*-butyraldehyde carried out as described above, were extracted from the aqueous solution with ether. Trial extractions showed that although the extraction was not quantitative, the results were sufficiently reliable for useful conclusions to be drawn about the nature of the products formed in oxidation.

The bulk of the ether was removed from the extracts by low-temperature distillation and the residues were analysed by gas–liquid partition chromatography using a katharometer detector. The 2-m column was packed with silicone fluid MS 550 and 10% stearic acid supported on celite[10] and hydrogen was employed as the mobile phase: with nitrogen carrier gas considerable difficulty was encountered due to peak-reversal. The column temperature was 110°.

With *n*-propanol and propionaldehyde, propionic and acetic acids were detected in the products. The ratio of the amounts of these acids was approximately the same for each compound and was constant over the range of strengths of dichromate studied.

Similar results were obtained with *n*-butanol and *n*-butyraldehyde; in this case the products were *n*-butyric, propionic and acetic acids.

Effect of acid strength on rate of reaction

A series of experiments was conducted in which the alcohol was oxidised at 100° by 0.5 *N* dichromate in 2.5%, 5%, 10% and 20% (v/v) sulphuric acid. Samples were taken from the reaction mixture at convenient intervals and the amount of dichromate consumed was determined as described above. Owing to uncertainties caused by delays in mixing and heating, the results were not considered sufficiently reliable for a detailed kinetic treatment, but it was clear that an increase in acid strength considerably speeded up the oxidation. A typical set of results is given below.

OXIDATION OF *n*-PROPIONALDEHYDE WITH 0.5 *N* $K_2Cr_2O_7$ IN H_2SO_4

TIMES FOR 90% COMPLETION OF REACTION

Acid strength (% v/v)	2.5	5	10	20
Time (min)	31	16	4	1

Intermediate products of the oxidation

These were determined by performing the oxidation with insufficient dichromate to convert the alcohol completely to acids. The following products were found:

n-propanol: propionaldehyde, acetic acid, *n*-propyl propionate and propionic acid, together with two other substances present only in trace amounts and believed to be acetals or hemiacetals.

n-butanol: *n*-butyraldehyde, *n*-butyric acid, *n*-butyl butyrate, propionic acid and acetic acid, together with a trace of an unidentified compound.

The products of the oxidation of the two esters were also studied and found to be:

n-propyl propionate: acetic and propionic acids.

n-butyl butyrate: acetic, propionic and *n*-butyric acids.

The results obtained suggested (see below) that valuable evidence concerning the position of oxidative attack, might be gained from a study of the oxidation products

of crotonaldehyde. This was partially oxidised using the same procedure and the products obtained included acetone, methyl ethyl ketone, propionic acid and traces of acetic acid.

DISCUSSION

The results of the stoichiometry experiments show clearly that this method is applicable to the determination of the single alcohols over quite wide ranges of reactant concentration with an accuracy under controlled conditions of approximately 2%. If necessary, the individual aldehydes could also be readily determined in the same way. As an analytical method, this procedure is simple and easily carried out by relatively unskilled personnel. The method is suitable for the determination of pure alcohols or aldehydes or their aqueous solutions.

During the oxidation process some fission of the carbon–carbon bonds takes place. From the relative amounts of oxygen consumed by the alcohol and by the corresponding aldehyde it is clear that the carbon–carbon bond is not broken until after the aldehyde stage is reached: that is, the reaction

$$RCH_2OH + O = RCHO + H_2O$$

proceeds stoichiometrically, but the subsequent reaction cannot be represented by the simple equation

$$RCHO + O = RCOOH$$

The overall reaction is facilitated by an increase in acid strength and it is believed that the carbon–carbon bond fission takes place via the enolisation of the aldehyde, a process which is well-known to be acid-catalysed[11].

The formation of propionic acid and only small amounts of acetic acid, during the oxidation of *n*-butanol and *n*-butyraldehyde leads to the conclusion that the major attack on the hydrocarbon chain occurs at the α-carbon atom. In the case of *n*-propanol and propionaldehyde the oxidative attack also presumably occurs at the α-carbon atom and the following outline mechanism is envisaged:

$$RCH_2CHO \overset{H^+}{\rightleftharpoons} RCH:CH(OH) \quad (1)$$

$$RCH:CH(OH) + O + H_2O = RCH(OH)CH(OH)_2 \quad (2)$$

$$RCH(OH)CH(OH)_2 = RCH(OH)CHO + H_2O \quad (3)$$

$$RCH(OH)CHO + O = RCOCHO + H_2O \quad (4)$$

$$RCOCHO + 2O = RCOOH + CO_2 \quad (5)$$

The enolisation of the aldehyde which is formed from the alcohol, is followed by the addition of two hydroxyl groups to the double bond and the α-hydroxy aldehyde hydrate thereby formed loses water to yield the α-hydroxy aldehyde. This compound is oxidised to the α-ketoaldehyde which in turn is decarboxylated to the lower acid.

According to this scheme, one mole of propionaldehyde consumes four atoms of oxygen. This is greater than the amount observed experimentally and it is clear that only some of the aldehyde reacts by this route and that the remainder is oxidised directly to the acid with the same number of carbon atoms. This mechanism is supported by several pieces of evidence:

(*a*) The overall reaction is acid-catalysed.

(*b*) The first detectable products in the oxidation of aldehydes by acid manganic pyrophosphate[8] or potassium nitrosyldisulphonate[6] are α-hydroxyaldehydes, which are easily oxidised further.

(*c*) During the oxidation of *n*- and isobutyraldehyde with acid dichromate solution, a cleavage occurs by α-oxidation of the enol form of these aldehydes[7].

The presence of acetic acid among the oxidation products of *n*-butanol and *n*-butyraldehyde may be explained by attack at the double bond of the enol form of the ketoaldehyde produced in (4), followed by a sequence of reactions similar to those postulated previously:

$$CH_3CH_2COCHO \rightleftharpoons CH_3CH:C(OH)CHO$$

$$CH_3CH:C(OH)CHO + O + H_2O = CH_3CH(OH)C(OH)_2CHO$$

$$CH_3CH(OH)C(OH)_2\,CHO = CH_3CH(OH)COCHO + H_2O$$

$$CH_3CH(OH)COCHO + 2O = CH_3COCOCOOH + H_2O$$

$$CH_3COCOCOOH + O = CH_3COCOOH + CO_2$$

$$CH_3COCOOH + O = CH_3COOH + CO_2$$

The alternative of β-oxidation of *n*-butyraldehyde is considered less likely, since this would presumably proceed via a preliminary dehydrogenation to crotonaldehyde; the oxidation products of crotonaldehyde include acetone, methyl ethyl ketone and only small quantities of acetic acid. The two ketones were not found among the products of *n*-butanol oxidation and the small amounts of acetic acid found were far less than were present in the butanol oxidation products.

Among the oxidation products of *n*-propanol by a deficiency of acid dichromate were propionaldehyde, acetic and propionic acids, and *n*-propyl propionate. It was shown that the oxidation of *n*-propyl propionate is considerably slower than the oxidation of *n*-propanol under the same conditions. Moreover, the relative amounts of the products formed, and their nature, show clearly that oxidation of the ester is preceded by hydrolysis to alcohol and acid. Similar conclusions were drawn from experiments on *n*-butyl butyrate (a produict of incomplete oxidaton of *n*-butanol) and it is therefore clear that the esters are not intermediates in the oxidation of the alcohols with excess dichromate, but are only formed when there is insufficient oxidant present to complete the conversion of alcohol to acids.

SUMMARY

The oxidation of *n*-propanol and *n*-butanol and the corresponding aldehydes by dilute acid potassium dichromate has been investigated. Some carbon–carbon bond fission occurs, and it has been shown that this takes place via the enol form of the aldehyde formed in the first stage of the oxidation. However, the proportion of this degradation is constant over a wide range of conditions and the method is capable of being used for the quantitative determination of simple aliphatic alcohols and aldehydes.

RÉSUMÉ

Les auteurs ont examiné l'oxydation du *n*-propanol et du *n*-butanol, ainsi que l'oxydation des aldéhydes correspondantes, au moyen du dichromate de potassium, en solution diluée. Cette méthode peut être appliquée au dosage d'alcools et d'aldéhydes aliphatiques simples.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Verlauf der Oxydation von *n*-Propanol und *n*-Butanol sowie der entsprechenden Aldehyde mit Kaliumbichromatlösung. Unter Berücksichtigung des beobachteten geringfügigen Abbaus der C-Kette (über die Enolform der Aldehyde) lässt sich diese Methode zur quantitativen Bestimmung einfacher aliphatischer Alkohole und Aldehyde verwenden.

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WO LIEGT DAS MINIMUM DER PUFFERUNG IN POTENTIOMETRISCHEN TITRATIONEN?

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"Je mehr sich eine Massanalyse ihrem Endpunkt nähert, desto grösser werden (auf gleiche Reagenszusätze bezogen) die messbaren Potentialänderungen; je weiter sie sich nachher vom Endpunkt entfernt, desto kleiner werden sie". Das ungefähr bieten, in Tabellen und Kurven die üblichen Darstellungen dieses Gebietes, und es ist unzweifelhaft richtig. Falsch dagegen ist die Schlussfolgerung: "Also muss das Maximum der Potentialänderung mit dem Aequivalenzpunkt zusammenfallen". Es müsste, wenn nicht in der nächsten Umgebung des Aequivalenzpunkt eine völlig andersartige Abhängigkeit zwischen der Differenz: Stoff minus Reagens und den Konzentrationen der potentialbestimmenden Ionen bestände: Die Differenz wird am Aequivalenzpunkt Null und die Konzentrationen werden es nicht. Ich schlage deshalb vor, die Gebiete fern vom Endpunkt, in denen die Konzentrationen aus der Differenz berechnet werden dürfen, die beiden "Aussenzonen" einer Titration zu nennen und das Gebiet nahe am Umschlag, wo dies nicht erlaubt ist, die "Innenzone". Wo liegt die Grenze? Etwa dort wo die Konzentration am Überschussreaktor rund hundertmal so gross wird wie die am Mangelreaktor, das dürfte eine für übliche Genauigkeitsansprüche befriedigende Antwort sein. (Akzeptiert man Reaktor für "Stoff oder Reagens", so ist das

Vorstehende ohne weitere Erklärung verständlich; das Gleiche gilt für einige weitere, im folgenden verwendete Ausdrücke).

Jede Betrachtung über die Steilheit der Potentialänderung am Endpunkt hat sich deshalb auf die Tatsache zu stützen, dass die Reaktorkonzentrationen hier nicht Null sind sondern eine angebbare Grösse haben (angebbar, wenn die nötigen Daten der Titration bekannt sind; sonst sage man "endlich"). Sie muss ferner die am Endpunkt erlaubte Annahme machen, dass das Gesamtvolumen im Vergleich mit der gerade hier sehr grossen Änderung der Reaktorkonzentrationen als konstant gelten darf; diese Annahme ist üblich, vielfach sogar für den ganzen Titrationsverlauf, wo sie besser unterbliebe. Ferner aber muss man in Rechnung stellen, und das wird leider vergessen: In den Titrationen schwacher Säuren oder Basen und in den Redoxbestimmungen steht an Stelle des Gesamtvolumens die Menge des am Aequivalenzpunkt vorhandenen Reaktionsproduktes und auch diese darf, ja muss sogar als konstant angesehen werden, wenn nur die nächste Umgebung dieses Punktes untersucht wird.

Für die logische und mathematische Behandlung des Endpunktproblems brauchen wir ferner Bezeichnungen für gemessene und gesuchte Grössen. Die im folgenden verwendeten scheinen mir, im Gegensatz zu manchen anderen, recht zweckmässig, weil sie prägnant sind; man wolle den letzten Abschnitt dieser Mitteilung beachten.

Nur analytisch messbare Konzentrationen, also von Reagentien, "Hilfsstoffen" (Säurezusatz) werden mit C_{index}, M oder N bezeichnet, Gleichgewichtskonzentrationen im betrachteten System dagegen mit a an Stelle von C_A oder $[A]$.

Da in der Massanalyse immer noch vorwiegend das Reagens mit Büretten gemessen wird, werden zugesetzte Reagensmengen mit v (wo nötig Indices) bezeichnet, auch wenn sie im g oder Coulomb gegeben sind; das ist erlaubt, wenn x, der gesuchte Reagenszusatz bis zur Aequivalenz mit dem vorhandenen Stoff, im gleichen Masse gegeben ist wie v; $|x - v|$ ist dann der Reaktorüberschuss, gleichgültig ob vor oder nach dem Aequivalenzpunkt. Allen Grössen, die sich auf den Aequivalenzpunkt beziehen, geben wir den Tiefindex o, weil sie zum Reaktorüberschuss Null gehören.

Wird es nötig, das Gesamtvolumen der titrierten Lösung einzuführen, so bezeichnen wir es mit V (Indices wie bei v); hier werden wir es nicht brauchen.

Potentiale seien E (Indices wie bei v) gleichgültig ob sie in mV gemessen sind (0.059 V erscheint unzweckmässig) oder als pC-Werte; der Faktor vor dem Logarithmus der Potentialformel ist ohne Bedeutung, solange nur die relative Grösse von Potentialschritten verglichen wird, und er fällt völlig heraus, sobald wir in der hier nötigen Rechnung den zweiten Differentialquotienten gleich Null setzen.

Diese Rechnung aber wird überraschend einfach, wenn wir nicht auf das Maximum der Potentialänderung sondern auf den reziproken Wert, das "Minimum der Pufferung" zielen, also den Wert d^2v/dE^2 aufsuchen; hier folgt die entsprechende Ableitung, zunächst für den Fall einer "symmetrischen" Titration, in der ein Mol Stoff sich mit einem Mol Reagens umsetzt. Die allgemeine Gleichung kann in diesem Falle entweder in der Form geschrieben werden

$$A + B \rightleftharpoons AB \qquad (1)$$

nämlich für Fällungen oder starke Säuren gegen starke Basen oder aber als

$$A + B \rightleftharpoons A' + B' \qquad (2)$$

für schwache Säuren oder Basen und die Redoxbestimmungen.

Im ersten Falle ist die Gleichgewichtsbedingung

$$a \cdot b = a_0 \cdot b_0 = a_0^2 = K \tag{3}$$

und im zweiten

$$\frac{a \cdot b}{a^1 \cdot b^1} = \frac{a_0 \cdot b_0}{a_0^1 \cdot b_0^1} = \left(\frac{a_0}{a_0^1}\right)^2 = K \tag{4}$$

Wenn wir so nahe am Aequivalenzpunkt bleiben, dass die Menge an Reaktionsprodukt als konstant gelten darf, dann dürfen wir in beiden Fällen

$$a \cdot b = a_0^2 = \text{konst.} \tag{5}$$

schreiben, nur ist diese Konstante im ersten Falle allein durch die Titrationsart gegeben und im zweiten durch Gleichgewichtskonstante der Reaktion und Konzentration der in jedem Einzelversuch entstehenden Reaktionsprodukte.

Wir nehmen nun an, dass einer Aequivalenzlösung eine sehr kleine Menge von einem der Reaktoren zugesetzt werde; es sei A. Ein Teil dieses Zusatzes $|x - v|$ wird die Konzentration an A erhöhen, der Rest aber wird sich mit B umsetzen also dadurch aus der Lösung verschwinden, dass er die Konzentration an B erniedrigt. Es ist daher (nach Gleichung (3) und (5))

$$|x - v| = (a - a_0) + (b_0 - b) = a - \frac{a_0^2}{a} \tag{6}$$

$$\frac{|x - v|}{a_0} = \frac{a}{a_0} - \frac{a_0}{a} = z - z^{-1} \tag{7}$$

womit wir die Potentialgleichung in der einfachen Form

$$E_v - E_0 = k \cdot \ln z \tag{8}$$

schreiben können; der numerische Wert von k darf, wie bereits gesagt, unbestimmt bleiben. Es ist dann

$$\pm \frac{dv}{dz} = z + z^{-2} \quad \text{und} \quad \frac{dE}{dz} = k \cdot z^{-1} \tag{9}$$

also

$$\pm k \frac{dv}{dE} = z + z^{-1} \tag{10}$$

und aus

$$\pm k \frac{d^2v}{dE^2} = z - z^{-1} = 0 \tag{11}$$

folgt mit Gl. (7) für das Reagensvolumen am Minimum der Pufferung: $x - v_m = 0$; es fällt also mit dem Aequivalenzvolumen zusammen.

Ergebnis: Das Maximum der Potentialänderung (Differentialquotient dE/dv), gleichbedeutend mit dem Minimum der Pufferung (dv/dE) tritt bei allen symmetrischen Titrationen im Aequivalenzpunkt auf. Symmetrisch sind die Titrationen von starken Säuren und Basen und "gleichwertige" Fällungen, die beide der Form $A + B \rightleftharpoons AB$ entsprechen (es entsteht nur ein Reaktionsprodukt), und mit zwei Reaktionsprodukten die Titrationen schwacher Säuren oder Basen und die gleichwertigen

Redoxbestimmungen, die zweckmässig $A_{ox} + B_{red} \rightleftharpoons A_{red} + B_{ox}$ formuliert werden.

Vorsichtshalber sei erwähnt, dass die Titration einer schwachen Säure (für die Base gilt Analoges) genau

$$(1-\mu)\,AH + \mu H_3O^+ + OH^- \rightleftharpoons (1-\mu)A^- + H_2O$$

zu formulieren ist, wobei μ ausserordentlich klein gegen eins ist; wo dies nicht der Fall ist, wäre der Verbrauch an Natronlauge am Maximum etwas grösser als der gelösten Säure entspricht, aber das kann nur unter Bedingungen der Fall sein, in denen die Endpunktsbestimmung aus dem Maximum der Potentialänderung wegen zu flachen Sprunges (siehe weiter unten) ohnedies versagt.

Wichtig dagegen ist die Divergenz zwischen dem vorstehendem Ergebnis und Befunden von KOLTHOFF UND FURMAN[1], die in symmetrischen Fällungen und bei starken Säuren und Basen das Maximum im Aequivalenzpunkt finden; in der Titration einer schwachen Säure[2] errechnen sie zwei Maxima, eins kurz vor und eins kurz nach dem Aequivalenzpunkt, und in ein/ein-wertigen Redoxtitrationen finden sie das Maximum immer kurz vor dem Aequivalenzpunkt. Darauf komme ich noch zurück; zunächst aber soll der Endpunktsfehler berechnet werden, der in unsymmetrischen Titrationen aller Art tatsächlich auftritt, was KOLTHOFF UND FURMAN nicht möglich war.

Es wäre gar nicht nötig gewesen, die symmetrischen Titrationen vorweg zu behandeln, denn es wird sich sofort zeigen, dass sie in der folgenden Entwicklung inbegriffen sind; aber diese wird nun derart erleichtert, dass wir einfach die gleiche Numerierung der Formeln mit dem Vorsatz u- verwenden wollen. Eine unsymmetrische Fällung kann

$$\alpha A^{\beta\pm} + \beta B^{\alpha\mp} \rightleftharpoons A_\alpha B_\beta \qquad \text{(u-1)}$$

und eine unsymmetrische Redoxbestimmung

$$\alpha A^{\beta\pm} + \beta B^{\alpha\mp} \rightleftharpoons \alpha A' + \beta B' \qquad \text{(u-2)}$$

geschrieben werden, wobei A' und B' selbstverständlich noch elektrische Ladungen tragen; hier kommt es nur auf die Zahl der ausgetauschten Ladungen (Wertigkeitswechsel) an.

Für den Verlauf der Titration ist nur der "Grad der Unsymmetrie", das ist der Quotient α/β wichtig; wir wählen die Bezeichnung so, dass α der grössere der beiden Koeffizienten ist, und setzen $\alpha/\beta = s$; damit wird $b_0 = a_0 \cdot s^{-1}$ und $\beta = \alpha \cdot s^{-1}$,

$$a^\alpha \cdot b^\beta = a_0{}^\alpha \cdot b_0{}^\beta = \text{konst.} \qquad \text{(u-5)}$$

wobei wieder in den Fällungen auf der rechten Seite unmittelbar die Gleichgewichtskonstante (Löslichkeitsprodukt) steht, bei den Redoxbestimmungen dagegen eine Funktion aus Gleichgewichtskonstante und Versuchsbedingungen, die konstant ist, solange sich die Menge an Reaktionsprodukt nicht ändert. Für die Fällungen gilt übrigens die völlig analoge Forderung, dass sich das Gesamtvolumen in nächster Nähe des Aequivalenzpunktes nicht merklich ändert; darauf kommen wir noch zurück.

Für einen kleinen Überschuss an A erhalten wir

$$v - x = (a - a_0) + s^{-1}(b_0 - b) = a - a_0(a_0/a)^s \qquad \text{(u-6)}$$

und, wenn wir wieder $a/a_0 = z$ setzen, so wird

$$\frac{v - x}{a_0} = z - z^{-s} \tag{u-7}$$

Differenzieren ergibt,

$$k \cdot \frac{dv}{dE} = z + sz^{-s} \tag{u-10}$$

$$k \cdot \frac{d^2v}{dE^2} = z - s^2 z^{-s} = 0 \tag{u-11}$$

$$v_m - x = (\overset{2}{s^{s+1}} - \overset{-2s}{s^{s+1}})a_0 \tag{u-12}$$

als Differenz zwischen dem Reagensvolumen am Minimum der Pufferung und dem Aequivalenzvolumen, genauer: der Konzentration, die diese Volumina im Endvolumen hervorrufen würden, bezogen auf die Aequivalenzkonzentration am Reaktor A als Einheit.

Für $s = 1$ wird die rechte Seite gleich Null: in symmetrischen Titrationen tritt kein "Umschlagsfehler" auf. Für $s \geqslant 1$ wird sie positiv: Der Umschlagsfehler führt zu einem berechenbaren Überschuss an dem Reaktor, der mit der grösseren Partikelzahl in die Reaktion eingeht. Zahlenmässig ist für $s = 1.33, 1.5, 2, 2.5, 3, 4, 5$, $(|x - v_m|)/a_0 = 0.56, 0.77, 1.19, 1.42, 1.54, 1.59, 1.64$.

Wird fünfwertiges Arsen (B) mit Titan(III)chlorid (A) titriert, so liegt, wenn die Bestimmung in normaler Salzsäure durchgeführt wird, der "Umschlag" bei einem Überschuss an Titan, der kleiner als 0.001% ist, weil die Umsetzung sehr vollständig also a_0/C ausserordentlich klein ist (C = Endkonzentration an $As^{+3} = Ti^{+4}$. Die gleiche Titration mit Kupfer(I)chlorid als Reduktor würde aber zu einem Mehrverbrauch von (rund) 0.2% führen). Man beachte: In den "Umformungstitrationen" ergibt sich der Fehler unmittelbar in Prozent der titrierten Menge.

Fällt man Chromat oder Oxalat mit Silbernitrat, so liegt der Mehrverbrauch an Reagens bis zum "potentiometrischen Umschlag" in der Grössenordnung von 10^{-4} mmol Reagens je ml also (rund) 0.1 ml zehntelnormaler Lösung auf 100 ml Endlösung. Es erscheint verfehlt, in "Kombinationstitrationen" den Fehler prozentisch anzugeben, denn das gilt immer nur für einen bestimmten Verbrauch an einem Reagens bestimmter Normalität und bestimmtem Endvolumen.

Der gleiche Unterschied zwischen Kombinationstitrationen (starke Säuren und Basen; Fällungen; also hier die Gleichungen (1) und (u-1)) und Umformungstitrationen (schwache Säuren oder Basen; Redoxbestimmungen; hier Gl. (2) und (u-2)) muss nun beachtet werden, wenn man die Zusammenhänge zwischen Reagenszusätzen und Potentialänderungen studiert. Das ist bei KOLTHOFF UND FURMAN nicht geschehen und damit erklären sich die Unterschiede zwischen ihren höchst verwunderlichen und den hier erhaltenen, durchaus einleuchtenden Ergebnissen.

Für die Kombinationstitrationen wird übereinstimmend gefunden: In den unsymmetrischen tritt der Umschlagsfehler auf, in den symmetrischen nicht. Wieso herrscht hier Übereinstimmung? Weil wir bei diesen Bestimmungen die Annahme machen müssen, dass beim Durchschreiten des Aequivalenzpunktes das Gesamt-

volumen nicht ändert, und diese Annahme ist selbst für den Gesamtverlauf der Bestimmung so üblich geworden, dass KOLTHOFF UND FURMAN sie sogar für eine Titration von Essigsäure und Ammoniak geben[3], bei der das Gesamtvolumen gar nicht in die Formeln eingeht.

Das gleiche gilt nun für alle Umformungstitrationen. Sie durchlaufen Puffergebiete und in diesen ist das Verhältnis von noch vorhandenem Stoff zu bereits gebildetem Reaktionsprodukt potentialbestimmend, unabhängig von dem Volumen, in dem sie gelöst sind. Nun kann die Menge gebildeten Reaktionsproduktes fern vom Aequivalenzpunkt und für endliche Reagenszusätze nicht als konstant gelten, wohl aber dürfen wir sie als konstant ansehen für differentielle Zusätze ganz dicht am Aequivalenzpunkt. Wir dürfen es nicht nur, sondern wir müssen es. Dagegen dürfen wir nicht, was bei KOLTHOFF UND FURMAN geschieht, dicht am Aequivalenzpunkt ("in der Innenzone") die Menge gebildeten Reaktionsproduktes gleich dem zugegebenen Reagens setzen: Sie ist kleiner. Wir dürfen nicht die Menge des noch frei vorhandenen Stoffes gleich Anfangsmenge minus zugegebenes Reagens setzen: Sie ist grösser.

Diese Irrtümer aber sind den Autoren unterlaufen, und sie verbinden sich mit einer — nach meiner streng persönlichen Überzeugung — sehr unzweckmässigen Wahl der Rechensymbole. Man sollte nicht die gesuchte Grösse mit c bezeichnen, zumal es sich nicht einmal um eine Konzentration handelt, und eine gemessene Grösse, den Reagenszusatz mit y. Wenn man dann noch (warum ist nicht gesagt) für die Differenz die Bezeichnung x einführt, dann muss man $c-y = x$ selbst dann noch gegenwärtig haben, wenn schliesslich eine Formel entwickelt wurde, in der links $y-c$ und rechts $-x^2$ als Faktoren vorkommen, die am Aequivalenzpunkt beide Null werden. Die ganzen Schlüsse bei KOLTHOFF UND FURMAN stützen sich aber auf die Annahme, dass nur die linke Seite Null werde und die rechte endlich bleibe.

Nach dem Vorstehenden dürfen wir wohl annehmen, dass der durch die Unsymmetrie von Titrierreaktionen entstehende Umschlagsfehler hier richtig erfasst wurde. Was ist damit gewonnen? Ich möchte vermuten: Dort wo das Gleichgewicht am Aequivalenzpunkt sicher feststeht, die analytische Verwendbarkeit von Reaktionen die bisher wegen Unsymmetrie und nicht sehr vollständiger Umsetzung nicht brauchbar waren. Umgekehrt: Dort, wo in komplizierten Reaktionen es fraglich erscheint, welche Zwischenstufen eigentlich am Aequivalenzpunkt das Potential bestimmen, sollten jetzt genaue analytische Versuche zur Aufklärung beitragen können. Sieht man das als einen gewissen Fortschritt an, dann wird man sich fragen, wodurch er möglich wurde. Sicher durch den Übergang von "Maximum der Potentialänderung" zu Minimum der Pufferung, der die Rechnung so unerhört vereinfacht und damit sichert. Dann aber durch das Bestreben, für jeden wichtigen Begriff einen möglichst zweckmässigen Ausdruck und ein möglichst einfaches und anschauliches Rechensymbol zu finden und, vor allem: Niemals die gleiche Bezeichnung für zwei verschiedene Begriffe zu benutzen. Ist das nicht selbstverständlich? In der Potentiometrie leider nicht. ERICH MÜLLER, den wir alle als unsern Lehrer auf diesem Gebiet zu betrachten haben, hat das Versehen begangen, Potentialsprung für die "Differenz der Normalpotentiale der elektrochemischen Teilvorgänge" zu verwenden (wo der Ausdruck schlecht passt) aber auch für den "auffallend grössten aller beobachtbaren Potentialschritte". Hier passt er ausgezeichnet, und ich möchte vorschlagen, die andere Grösse "Potentialabstand der Teilreaktionen" zu nennen.

"Fehler" sollte nur verwendet werden, wo die Abweichung vom theoretischen Wert

"gerichtet" ist, wie hier beim "Umschlagsfehler" oder einer aus bestimmten Gründen nicht genau stöchiometrisch verlaufenden Titrierreaktion. Handelt es sich dagegen um die unvermeidlichen Schwankungen der Einzelversuche, die durch $\pm n\%$ (oder mmol/ml) zum Ausdruck kommen, dann sollte man vielleicht "Unsicherheit" oder "Schwankungsbreite" sagen. Die Beispiele liessen sich beträchtlich vermehren.

Ich habe mich hier bemüht, Ausdrücke und Zeichen zu verwenden, die ich für eindeutig und klärend, aber sicher nicht für die besten aller möglichen halte. Sollte nicht eine Diskussion *sine ira* und eine Einigung auf eine von allen zu benutzende Bezeichnungsweise möglich sein?

ZUSAMMENFASSUNG

In allen symmetrischen Titrationen fällt das Minimum der Pufferung, das ist der Differentialquotient dv/dE auf den Aequivalenzpunkt. Für unsymmetrische Titrationen konnte die Differenz zwischen Minimum- und Aequivalenzvolumen berechnet werden; die Zahlenwerte werden angegeben.

SUMMARY

For all symmetrical titrations the minimum of the buffer capacity, *i.e.* the differential quotient dv/dE, coincides with the equivalence point. For asymmetrical titrations the differences between the minimum and the equivalence volumes have been calculated; the numerical values are given.

RÉSUMÉ

Dans tous les titrages symmétriques le minimum du pouvoir tampon coïncide avec le point d'équivalence. Pour les asymmétriques, les différences entre le minimum et le volume d'équivalence ont été calculées et sont données.

LITERATUR

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QUANTITATIVE CHROMATOGRAPHIC ANALYSIS USING RECTIFIED RADIO FREQUENCY METHODS
PART II. FLUORIDE, CHLORIDE, BROMIDE AND IODIDE

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INTRODUCTION

In an earlier publication[1] the quantitative analysis of mixtures of lithium, sodium and potassium ions by chromatographic and radio-frequency techniques has been described. In this paper the method is extended to the halide ions.

The technique is as follows. Fluoride, chloride, bromide and iodide present as their sodium salts are separated by paper chromatography using a new solvent mixture. The separated zones are detected by the radio-frequency method of BLAKE[2]. The bands are then cut out and the salt present is extracted from the paper with a known volume of water. The impedances of the solutions so obtained are then measured and compared with those of standard solutions prepared in the same way. The impedance measurements are made by means of BLAKE's conductimetric tube[2].

EXPERIMENTAL

Materials

The analytical grade quality sodium salts were used, the fluoride and chloride being dried and weighed directly. The bromide was standardised by the Mohr titration method[3] and the iodide solution by titration with standard potassium iodate[4]. The solutions were made up with distilled water and contained the following amounts of halide ion per 100 ml: fluoride, 1.847 g; chloride, 2.331 g; bromide, 1.516 g; iodide, 1.989 g.

Whatman No. 3 chromatography paper (cut in strips 2.6 × 60 cm) was found satisfactory. The solvent consisted of a 4:2:1 mixture (by volume) of acetone, pyridine and water, and the organic constituents were used without further purification. The chromatographic separation was carried out in large glass tubes which accommodated two chromatograms per tube.

Method

The solutions were placed on a pencil line 2.6 cm from the lower end of the paper by means of an Agla micrometer syringe (Burroughs Wellcome and Co. London). The range covered was from 0.2–2 mg of halide ion. For each quantity, 20 chromatograms were prepared, 4 being of the mixed halides and 4 each of the individual halides to

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provide the standards. The papers were suspended from hooks in the chromatography tubes and the ends immersed in the developing solvent to a depth of about 1 cm. After 24 h the solvent front had moved at least 44 cm up the paper. The slight colouration present in the pyridine of the solvent moved with the solvent front and so provided a permanent record of the distance moved. The chromatograms were dried,

TABLE I

Ion	Mean meter readings in μA				mg of ion		
	Standard	Unknown	Maximum deviation from mean	Average deviation	Present	Found	% Error
Fluoride	9	9	< ± 1	< ± 1	0.20	0.20	< 1
Fluoride	28	27	< ± 1	< ± 1	0.50	0.52	4
Fluoride	42	42	< ± 1	< ± 1	0.80	0.80	< 1
Fluoride	54	55	± 1	< ± 1	1.10	1.13	3
Fluoride	65	65	± 2	± 1	1.40	1.40	< 1
Fluoride	75	76	± 3	± 1	1.70	1.73	2
Fluoride	82	82	± 3	± 1	2.00	2.00	< 1
Chloride	8	8	± 1	± 1	0.20	0.20	< 1
Chloride	20	22	< ± 1	< ± 1	0.50	0.52	4
Chloride	35	34	± 1	< ± 1	0.80	0.79	1
Chloride	45	44	< ± 1	< ± 1	1.10	1.07	3
Chloride	54	53	± 1	± 1	1.40	1.38	2
Chloride	61	62	± 1	± 1	1.70	1.72	1
Chloride	71	70	± 1	± 1	2.00	1.99	< 1
Bromide	2.9	1.9	± 0.4	± 0.1	0.20	0.13	35
Bromide	6.9	6.3	± 0.6	± 0.3	0.50	0.45	10
Bromide	10.1	10.8	± 1.9	± 1.0	0.80	0.86	8
Bromide	13.0	13.3	± 0.1	± 0.1	1.10	1.13	3
Bromide	16.0	14.6	± 0.6	± 0.3	1.40	1.26	10
Bromide	19.4	18.7	± 1.4	± 0.7	1.70	1.65	3
Bromide	22.4	21.5	± 1.4	± 0.7	2.00	1.91	4
Iodide	4.6	4.8	± 1.1	± 1.0	0.50	0.52	4
Iodide	7.1	7.4	± 1.6	± 0.9	0.80	0.77	4
Iodide	11.8	10.3	± 0.8	± 0.6	1.10	1.04	6
Iodide	13.9	14.2	± 1.8	± 0.9	1.40	1.47	5
Iodide	15.8	16.7	± 0.6	± 0.3	1.70	1.72	1
Iodide	19.5	20.0	± 0.8	± 0.5	2.00	2.06	3

then conditioned for 30 min in an atmosphere of relative humidity about 90% to facilitate finding the bands with the zone detector. After cutting out, the spots were extracted with 25 ml of distilled water. The resulting solutions were allowed to come to temperature in a constant temperature bath (20 ± 0.3°) and their impedances then measured with the conductimetric tube. The readings for the iodide and bromide solutions were taken with a galvanometer (sensitivity 7.3 mm per μA). For the more concentrated chloride and fluoride solutions a less sensitive microammeter could be employed.

The calibration curves were constructed by plotting the meter readings against quantity of ion present for the standards, and the unknowns then read off from the graphs. The results obtained are given in Table I.

DISCUSSION

Consideration of the results leads to the following range of the analyses:

Ion	*Range (mg)*	*Average % accuracy*
Fluoride	0.50–2.00	2
Chloride	0.50–2.00	2
Bromide	0.50–2.00	6
Iodide	0.50–2.00	3

It is reasonable that the fluoride and chloride analyses should be the more accurate, since for a given volume they gave solutions of the greater molarity. All other errors being equal, the greater the molarity the greater the meter readings, with consequent increased accuracy[1]. Further, the fluoride and chloride gave sharper bands on the paper and so were more readily located. The following diagram (Fig. 1) shows a typical separation curve for approximately 1-mg amounts of each halide ion.

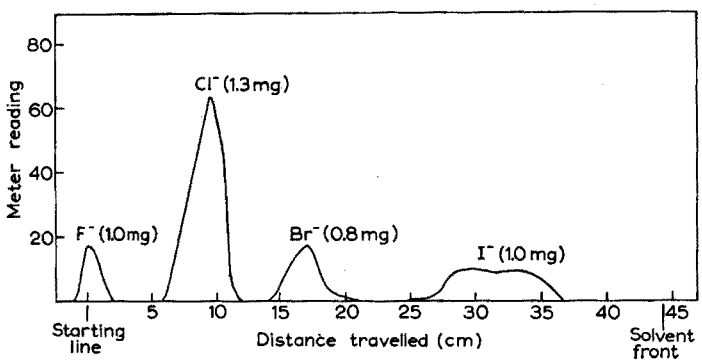

Fig. 1. Typical zone detector curve of mixed sodium fluoride, chloride, bromide and iodide after chromatographic separation.

The bromide and iodide bands were difficult to locate with certainty, particularly the iodide band, which did not form a peak. When making impedance measurements their solutions required the use of a more sensitive meter. This increased the difficulty in repeating readings as the more sensitive meter picked up readings arising from the "background" of the paper itself. It was found that the paper over which the solvent had travelled, itself gave a reading of *ca.* 0.3 μA per cm per 25 ml. Consequently, different band lengths had different "background" errors associated with them. Attempts to make a correction for the reading due to the "background" did not improve the accuracy, probably because this reading was not uniform along the paper length. The halide ion separations were carried out in tubes instead of large tanks, since the path length required for a separation was too great for the tanks available. Consequently there was not overall uniformity in the length travelled by the solvent front on each paper. This produced a greater variation in the band lengths of repeat chromatograms and therefore in the meter readings of the solutions obtained. The technique employed in the analysis of the halide ions differed slightly from that

employed in the earlier paper on the alkali metals. In preparing the chromatograms a micrometer syringe was used to deliver the small volumes; and in extracting the separated bands, a constant volume of water was used throughout. Both changes resulted in fewer operations, and hence a more rapid analysis.

A new solvent mixture was employed in the chromatography and a sample of the type of separation curve obtained is shown in Fig. 1. The R_F values of the peaks with this solvent have been determined as follows.

Ion	R_F
F^-	0
Cl^-	0.20 ± 0.03
Br^-	0.36 ± 0.06
I^-	0.69 ± 0.06

Each R_F determination is the mean of 5 values. The iodide band did not form a peak and instead the centre of the band was taken for the R_F measurement. The usual spot test techniques were applied to identify the zones.

ACKNOWLEDGEMENT

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SUMMARY

A new developing solvent is described for the paper chromatographic separation of sodium fluoride, chloride, bromide, and iodide. The separated ion zones are located by the BLAKE Zone Detector, and the amount of halide ions present determined by measurement of the impedance of their respective aqueous extracts.

RÉSUMÉ

Une méthode est décrite pour la séparation par chromatographie sur papier des fluorure, chlorure, bromure et iodure de sodium. Les zones sont localisées par le détecteur de zones BLAKE et la teneur en halogénures présents est déterminée par mesure de l'impédance de leurs extraits aqueux respectifs.

ZUSAMMENFASSUNG

Beschreibung einer papierchromatographischen Methode zur Trennung und Bestimmung von Natriumfluorid, -chlorid, -bromid und -jodid. Der Nachweis der einzelnen Zonen geschieht nach der Radio-Frequenz Methode von BLAKE. Die einzelnen Zonen werden herausgeschnitten, mit Wasser extrahiert und der Gehalt an Salz durch Messung der Impedanzen festgestellt.

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DETERMINATION OF RHODIUM BY THERMAL NEUTRON ACTIVATION ANALYSIS USING γ-RAY SPECTROMETRY

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INTRODUCTION

In a recent review article BEAMISH[1] pointed out the lack of satisfactory analytical methods for trace amounts of rhodium. Two colorimetric determinations[2] are applicable in the 25–200 μg region but these are complicated methods requiring detailed separation procedures. Thermal neutron activation with gross β-ray measurement has been used in this laboratory[3,4] to determine trace rhodium content in samples such as meteorites. γ Spectrometry has also been attempted elsewhere[5] but there was a need for a general evaluation of this method.

The concept of analysis by nuclear reaction is well established and was summarized a number of years ago by BOYD[6]. As applied to rhodium, the nuclear reactions, $^{103}Rh(p,n)^{103}Pd$, $^{103}Rh(n,\alpha)^{100}Tc$, and $^{103}Rh(n,\gamma)^{104}Rh + {}^{104m}Rh$ are the principal reactions available to the analyst for qualitative and quantitative analysis. The (p,n) reaction requires a high-energy positive-ion accelerator and is relatively insensitive from a practical view because of the 17-day ^{103}Pd product. The (n,α) reaction is more adaptable from the product half-life consideration but presently available sources of the fast neutrons required for this reaction, limit the sensitivity to approximately 10 p.p.m. As neutron generators are improved, this reaction will become more important.

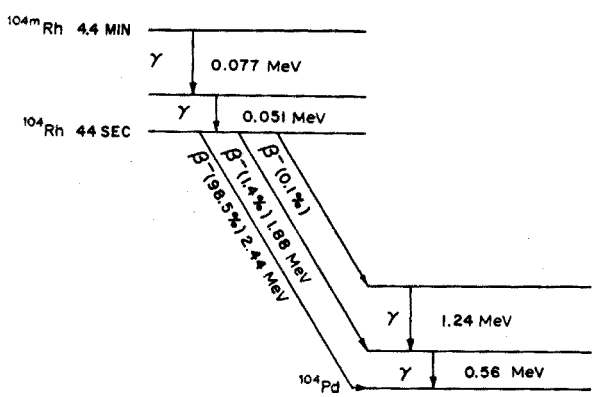

Fig. 1. Decay scheme of ^{104}Rh isomers[8].

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At the present time, however, the (n,γ) reaction is the most important for activation analysis. This reaction has favorable cross-sections, produces radioactive products with convenient half-lives and can be run with any source of thermal neutrons[7]. Indeed rhodium is one of the elements for which thermal neutron activation is optimum.

When irradiated with thermal neutrons, the naturally-occurring mono-isotopic ^{103}Rh nuclei absorb neutrons to form an unstable configuration. Excess energy is emitted from this configuration mainly by the emission of prompt γ rays until the nuclei reach the ground state of ^{104}Rh or an isomeric state ^{104m}Rh. The probability is greater for the formation of ^{104}Rh than it is for ^{104m}Rh by a factor of 137.0 to 11.8 (*i.e.* the ratio of the reaction cross-sections). These isotopes are radioactive and decay to the ground state of ^{104}Pd by the emission of β and γ rays. The decay of these isomers is given in Fig. 1[8].

The analyst can make use of the short-lived isomer (42- or 44-sec depending upon the reference[8,9]) in a non-destructive method or can take advantage of the equilibrium between the two species (with an effective half-life of 4.4 min) to separate rhodium chemically from its matrix prior to measurement. This paper describes a procedure for sub-microgram quantities of rhodium based on each of these two approaches using the Ford Nuclear Reactor at the University of Michigan.

EXPERIMENTAL

Apparatus and reagents

Samples were irradiated in the Ford Nuclear Reactor of the Phoenix Memorial Laboratory at the University of Michigan. Use was made of the pneumatic tube system[10] which permitted short and precisely-timed irradiations coupled with rapid delivery of the samples into and out of the neutron fields. Samples were delivered within 3 sec by this system to a hood in the neighboring radioisotope laboratory. Neutron fluxes, at the center of the irradiating positions, varied from $9.9 \cdot 10^{11}$ to $1.3 \cdot 10^{12}$ n cm^{-2} sec^{-1}. Relative values of neutron flux were determined for each sample by activation of gold foils. Measurement of these gold foils in a calibrated scintillation well counter permitted normalization of the results for all irradiations to a flux level of 10^{12} n cm^{-2} sec^{-1}.

A second pneumatic tube system was used to transfer the irradiated samples from the laboratory hood to the sodium iodide detector of the scintillation spectrometer. This system uses 0.5 in. i.d. aluminum tubing and a vacuum cleaner for suction. The sample is transported to the detector in 2 sec and there triggers circuits which are designed to start the analyzer when the sample is in position for counting.

Radioactivity assays were made by γ-ray spectrometry using a dual-memory, 100-channel, vacuum tube, Radiation Instruments Development Laboratory pulse height analyzer coupled with a 3 in. $\times$ 3 in. NaI(Tl) detector. Resolution for this particular phototube and crystal was 10.8%. Dead time of the analyzer system varied with the strength of the samples and was recorded during the counting operation.

All reagents were C.P. or analyzed reagent grade and were used without further purification.

Non-destructive method using 44-sec ^{104}Rh

Samples containing varying amounts of rhodium ($RhCl_3$ in 1 N HCl) were sealed

in medical grade polyethylene tubing, enclosed in a 1 in. × 3 in. polyethylene "rabbit" and irradiated in a thermal neutron flux of $\sim 10^{12}$ n cm^{-2} sec^{-1} for 42 sec. At the end of the irradiations, the samples were returned to the laboratory, repackaged, and sent to the scintillation detector. The elapsed time from the end of irradiation to the start of the counting period varied from 19 sec to 54 sec.

γ Radiations from the samples were detected, analyzed, and stored for 1 min in the memory of the analyzer. This information was then recorded both graphically on an X-Y recorder and in digital form by a Hewlett-Packard printer. The number of scintillation counts/min in the 0.56-MeV photopeak is proportional to the weight of rhodium present. All counts were normalized for decay (to the end of irradiation), for analyzer dead time (to 0%), and for neutron flux (to 10^{12} n cm^{-2} sec^{-1}). Background radiations from other activities were eliminated by an extrapolation of the base line under the photopeak as illustrated in Fig. 2.

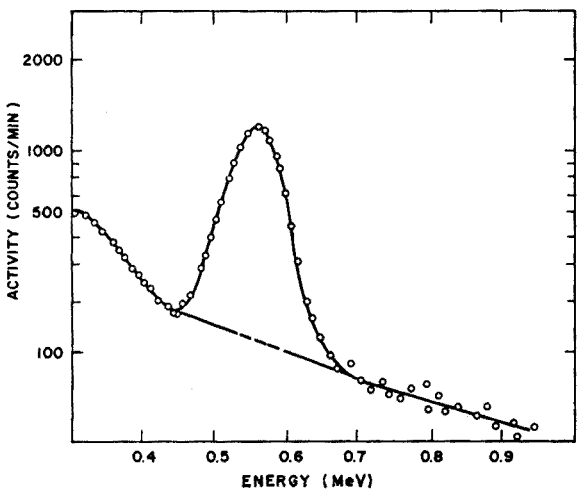

Fig. 2. γ-Ray spectrum of ^{104}Rh (from 0.3 to 1.0 MeV) showing extrapolation of base line under 0.56 MeV photopeak to eliminate contribution of other activities. Sample: 0.25 μg Rh as $RhCl_3$ in HCl; 42-sec irradiation; 23-sec transfer time; 1-min counting time; 7% dead time; 9,167 counts in peak; A_0 = 13,398 counts/min.

Destructive method using 4.4-min ^{104m}Rh

Rhodium samples, with and without other elements, were packaged as described above and irradiated for 5 min. When returned to the laboratory, they were cut open and cautiously added to ten times their weight of previously heated sodium peroxide. The melt was heated for 1 min, cooled by dipping the outside of the nickel crucible in cold water while rotating the crucible to coat the inside, and dissolved by cautiously adding 20 ml of concentrated hydrochloric acid.

5 ml of $RhCl_3$ carrier solution (1 mg/ml in 1 N HCl), 1 ml of 10% tartaric acid, and 8 ml of pyridine were added and the solution was filtered into a separatory funnel[11]. An additional 5 ml of 6 N HCl was used to rinse the crucible and filter. The solution was then made basic with 15 ml of 12 N sodium hydroxide. After thorough mixing for 1 min the pyridine layer was separated. An aliquot was then measured by γ-ray spectrometry. The chemical yield of the separation procedure was determined by measuring the pyridine–rhodium complex absorbance at 440 mμ. The counts in the 0.56-MeV photopeak were corrected for elapsed time, analyzer dead time, neutron flux variations, and for the chemical yields.

RESULTS AND DISCUSSION

Calibration data for the non-destructive analysis of rhodium were obtained by 42-sec irradiations of known amounts of the element and subsequent analysis of the γ-ray scintillation spectra. Part of such a γ-ray spectrum from 0.3 MeV to 1 MeV obtained with 0.25 μg of rhodium is shown in Fig. 2.

Table I gives the results of these calibrations. The method is probably accurate to within $\sim \pm 6\%$ over the weight range of 0.1 to 1 μg of rhodium. In the range of 0.01

TABLE I

CALIBRATION DATA FOR NON-DESTRUCTIVE RHODIUM ANALYSIS BY THERMAL NEUTRON ACTIVATION ANALYSIS (10^{12} n cm^{-2} sec^{-1}) USING 44-sec ^{104}Rh

Sample	*Rhodium (μg)*	*Irrad. time (sec)*	*Transfer time (sec)*	*A_0 Photopeak[a] (counts min^{-1} at end of irrad.)*	*Specific activity (counts min^{-1} μg^{-1})*
$RhCl_3$ in 1 N HCl	0.01	42	19	575[b]	57,500
$RhCl_3$ in 1 N HCl	0.10	42	32	5,391	53,910
$RhCl_3$ in 1 N HCl	0.25	42	23	13,398	53,592
$RhCl_3$ in 1 N HCl	0.50	42	54	27,525	55,050
$RhCl_3$ in 1 N HCl	0.75	42	25	41,340	55,120
$RhCl_3$ in 1 N HCl	1.00	42	28	57,074	57,074
				Average	55,374 $\pm$ 2.6%[c]

[a] Corrected for analyzer dead time and neutron flux variation.
[b] Average of three determinations. All other values are from a single determination.
[c] Error is "standard deviation" of the six values. Statistically the higher counting values of A_0 are more significant and hence some weighting factor should probably be used in determining the error. Such a procedure would tend to reduce the value of this error.

TABLE II

ANALYSIS OF STANDARD RHODIUM SAMPLES BY NEUTRON ACTIVATION ANALYSIS

Sample	*Irradiation time*	*Matrix*	*Chemical separation*	*μg Rh*	
				Added	*Found*
1	42 sec	H_2O–HCl	None	0.01	0.011[a]
2	42 sec	H_2O–HCl	None	0.01	0.009[a]
3	42 sec	H_2O–HCl	None	0.01	0.012[a]
4	42 sec	H_2O–HCl	None	0.01	0.013[a]
5	42 sec	H_2O–HCl	None	0.01	0.012[a]
6	42 sec	H_2O–HCl	None	0.01	0.011[a]
7	42 sec	H_2O–HCl	None	0.10	0.095[a]
8	42 sec	Silica gel	None	0.50	0.53[a]
9	42 sec	Silica gel	None	1.00	1.02[a]
10	5 min	H_2O–HCl	Pyridine extraction	0.10	0.08[b]
11	5 min	H_2O–HCl	Pyridine extraction	0.50	0.48[b]
12	5 min	H_2O–HCl[c]	Pyridine extraction	1.00	1.10[b]
13	5 min	H_2O–HCl[c]	Pyridine extraction	1.00	1.02[b]
14	5 min	H_2O–HCl[c]	Pyridine extraction	1.00	1.08[b]
15	5 min	Silica gel	Pyridine extraction	1.00	1.04[b]

[a] Based on 55,374 counts min^{-1} μg^{-1} Rh at 10^{12} n cm^{-2} sec^{-1}
[b] Based on 3,698 counts min^{-1} μg^{-1} Rh at 10^{12} n cm^{-2} sec^{-1}
[c] Contained approximately 100 p.p.m. K, Sr, Ce, Zr, Ru, Pd, Ag, Zn, In, Sb, and Re

to 0.1 μg, this accuracy is probably within $\sim \pm 20\%$. These data, along with the results of several standard sample analyses, are given in Table II. The average time per analysis is 7 min for this non-destructive method using the short-lived radioactive isomer.

It can be seen from Table II that at the 0.50-μg level of rhodium even such a "problem" matrix as silica gel offers little trouble in this non-destructive method since the 44-sec isomer has such a high sensitivity for activation analysis. One might, however, expect that elements such as silver, iodine, bromine, tungsten, arsenic, antimony, copper, zinc, and others with γ-ray peaks near 0.56 MeV might interfere if present in the matrix in much larger concentrations than the rhodium (see Fig. 27 of ref. [12] for a graph of relative calculated sensitivities).

When such interferences are found in samples, a chemical separation is necessary before a radioactive assay can be made. A calibration curve for rhodium analysis was prepared using the separation techniques of sodium peroxide fusion and pyridine extraction to isolate the 4.4-min ^{104m}Rh pure enough for γ-ray spectroscopy. These calibration data are given in Table III and the results for several standard samples analyzed by this method are included in Table II. The method is probably accurate to within $\sim \pm 20\%$ over the range of 0.10 to 1 μg of rhodium. The average time per analysis using the 4.4-min isomer is 20 min including 5 min for the irradiation.

TABLE III

CALIBRATION DATA FOR RHODIUM ANALYSIS BY THE PYRIDINE EXTRACTION METHOD USING THE 4.4-min ^{104m}Rh FOR THERMAL NEUTRON ACTIVATION ANALYSIS (10^{12} n cm^{-2} sec^{-1})

Sample	*Rhodium (μg)*	*Irrad. time (min)*	*Time for chemistry (min)*	*A_0 Photopeak[a] (counts min^{-1} at end of irrad.)*	*Specific activity (counts min^{-1} μg^{-1})*
$RhCl_3$ in 1 N HCl	0.10	5	8.3	343[b]	3,430
$RhCl_3$ in 1 N HCl	0.50	5	7.1	1,880	3,760
$RhCl_3$ in 1 N HCl	1.00	5	7.8	3,903	3,903
					Average 3,698 $\pm$ 5.4%[c]

[a] Corrected for analyzer dead time, neutron flux variation, and chemical yield.
[b] Average of three determinations. Other values are from a single determination.
[c] Error is "standard deviation" (see note c, Table I)

The short-lived ^{104}Rh also has a γ-ray peak at 1.24 MeV. In this region of the γ spectrum there are fewer potential interferences (indium, silicon, argon, and cadmium being the principal ones[12].) However, since the sensitivity of the peak is less than that of the 0.56-MeV peak by a factor of $\sim$ 20, the lower-energy peak will probably be used for most non-destructive analyses.

A glance at the decay scheme of these rhodium isomers (Fig. 1) shows that a large percentage (98.5%) of the decay is by β emission directly to the ground state rather than through the 0.56-(1.4%) or 1.24-(0.1%) MeV γ rays. Thus, activation analysis of rhodium by measuring the high-energy β ray of ^{104}Rh should give considerably higher sensitivities[13] than reported above. Unfortunately β-ray measurement cannot be made as discriminating as γ-ray spectrometry and hence samples with few other activating impurities would probably be required to utilize the very high sensitivity of the 44-sec ^{104}Rh. Suitable designs of regular or low-background β counting equipment could, however, be used with good radiochemical separations

(as developed above or adapted from ref. [14]) to lower the limit to at least 10^{-9} g with thermal neutron fluxes of 10^{12} n cm^{-2} sec^{-1}. Similar procedures should give sensitivities approaching μg levels of rhodium with low cost neutron generators such as are now available[12,15].

For most practical situations requiring high sensitivity, however, it would appear that at present the non-destructive method using a reactor and γ-ray spectrometry will be of most importance because of its simplicity.

ACKNOWLEDGEMENTS

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SUMMARY

Trace amounts of rhodium have been determined by thermal neutron activation analysis using both destructive and non-destructive methods. With a neutron flux of 10^{12} n cm^{-2} sec^{-1} the lower limits of detection are about 0.1 μg and 0.01 μg, respectively. A rapid sodium-peroxide fusion followed by a pyridine extraction was used in the destructive method to separate the 4.4-min ^{104m}Rh from its matrix. The 44-sec ^{104}Rh was used in the non-destructive method. Both radioactive isomers were measured by γ-ray spectrometry with a multichannel pulse height analyzer. The average time required per non-destructive analysis was 7 min while the chemical method averaged 20 min.

RÉSUMÉ

Des traces de rhodium ont pu être analysées par activation au moyen de neutrons thermiques, en utilisant soit une méthode destructive (fusion avec peroxyde de sodium et extraction dans la pyridine pour séparer ^{104m}Rh (4.4 min), soit une méthode non-destructive (utilisant ^{104}Rh (44 sec)). Ces deux isomères radioactifs ont été mesurés au moyen d'un spectromètre γ à plusieurs canaux.

ZUSAMMENFASSUNG

Spurenmengen von Rhodium können durch Aktivierung mit thermischen Neutronen bestimmt werden unter Anwendung von destruktiven (Aufschluss mit Natriumperoxyd und Isolierung des 4.4-Min 104-Rh) oder nicht destruktiven Verfahren durch Verwendung von 44-sec 104-Rh. Die beiden radioaktiven Isomere werden mit einem Mehrkanal-Gammastrahlen Spektrometer gemessen.

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DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC FLUORINE COMPOUNDS

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The determination of carbon and hydrogen in fluorinated materials has long been a subject of interest in this Department. Because a very wide variety of substances is submitted for analysis, previous attention has been concentrated on reliable slow procedures for this determination. However, with increasing demand for analyses, it became necessary to develop a faster method. The present paper describes a method which is generally applicable and in which a single analysis in series takes only 30 min.

The slow methods which were applied here previously were those of BELCHER AND GOULDEN[1] and MCCOY AND BASTIN[2]. In the former method, the silicon tetrafluoride formed during the combustion over a platinum catalyst is removed on a layer of sodium fluoride pellets at 270°. In the latter method, magnesium oxide pellets placed at each end of a copper oxide layer serve to remove fluorine from the combustion products, the whole filling being maintained at 900°. Magnesium oxide was originally suggested for this purpose by THROCKMORTON AND HUTTON[3] and has also been used by GEL'MAN AND KORSHUN[4]. Several other absorbents have been recommended for the removal of fluorine-containing combustion products (see[5]) but the sodium fluoride and magnesium oxide methods seemed to be the most convenient and reliable.

Comparative tests of the two methods for routine work have been made in these laboratories over a period of several years. In the magnesium oxide method the copper oxide was replaced by a platinum catalyst; otherwise the procedure was as specified by MCCOY AND BASTIN. Both methods proved quite satisfactory, the carbon values being slightly better with the sodium fluoride absorbent and the hydrogen values better with the magnesium oxide absorbent. The combustion tubes and their packings lasted for 2–3 months of constant use but, although the platinum catalyst in the BELCHER AND GOULDEN method required cleaning about every 2 weeks, the catalyst in the magnesium oxide procedure needed no treatment during the lifetime of the tube. It was therefore concluded that the platinum probably served no useful purpose in this method, and that magnesium oxide alone should be equally satisfactory.

In recent years, much work has been done on the development of rapid methods for determination of carbon and hydrogen. The empty tube method of BELCHER AND INGRAM[6] has been modified for the analysis of fluorinated materials[7] by placing a layer of sodium fluoride pellets after the combustion chamber. But the combustion tube is expensive so that one hesitates to expose it constantly to the attack of highly fluorinated materials, and it was therefore considered better to use conventional

combustion tubes. The combustion catalysts of KÖRBL and VEČEŘA — the silver permanganate decomposition product[8] and cobaltic oxide[9] respectively — were examined for fluorinated compounds; both seemed quite satisfactory for compounds containing little fluorine, but highly fluorinated substances were only partially oxidised[10]. Other studies on these catalysts[11] suggested that the speed of the methods depended almost as much on the short length of the combustion tube as on the efficiency of the catalyst.

It therefore seemed probable that a packing of magnesium oxide as a fluorine absorbent and combustion aid in a short combustion tube would provide a rapid and extremely economical method for the determination of carbon and hydrogen in fluorinated materials. This proved to be true and a method of general applicability has been developed. The sample is burned over magnesium oxide at 800–850° in a combustion tube of conventional design but with an overall length of only 36 cm. Halogens other than fluorine, and sulphur are removed on silver gauze, and nitrogen oxides in an external absorber. Carbon dioxide and water are determined gravimetrically in the conventional way.

EXPERIMENTAL

Apparatus

A diagram of the apparatus is shown in Fig. 1. The combustion tube (D) of transparent top-grade silica has a total length of 36 cm and an inner diameter of 9 mm, and is fitted with a side-arm and 3 cm beak end in the normal manner. The tube between the side-arm and the stopper is extended to 5 cm to avoid any danger of heating the

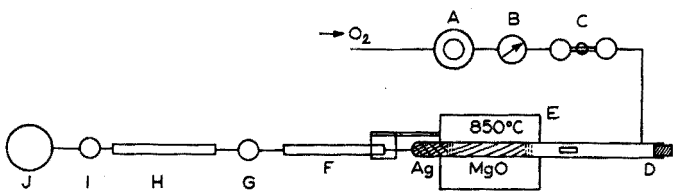

Fig. 1. Line diagram of apparatus.

rubber bung during the preliminary heating of highly volatile liquids. The furnace (E) is 15 cm long and its temperature is controlled at 820–850° by a variable transformer. When not in use, *e.g.* overnight, the furnace is maintained at 500–600°. A small attachment from the furnace serves to heat the capillary of the water absorption tube and so prevent condensation of moisture.

Sample volatilization is done with a Bunsen burner with a short nickel sheath around the combustion tube.

The oxygen flow of 12 ml/min is maintained by a pressure head of sulphuric acid (A), controlled by a simple needle valve (B) and checked by means of a reversible aspirator bottle (J)[1] at the end of the train. The oxygen is purified by passing through anhydrone, soda-asbestos and anhydrone in a glass-stoppered U-tube with a stopcock between the two limbs (C). (No preheater is used, since the oxygen and the supply lines in this laboratory are known to be very free of contamination).

Pregl-type absorption tubes are used for the absorption of water (F) and carbon

dioxide (H). Nitrogen oxides are absorbed in manganese dioxide (G) placed between the Pregl absorption tubes[1,6]. A guard tube (I) containing anhydrone and soda asbestos is placed before the aspirator bottle. Connections in the train before the combustion tube are made with aged rubber tubing and other connections with thick-walled impregnated rubber or neoprene tubing.

Preparation of magnesium oxide pellets

"Light" magnesium oxide and "heavy" magnesium oxide (B.D.H. Ltd. or May and Baker, Ltd.) in the proportion of 1 : 3 are mixed to a paste with water and dried, with occasional tamping, at about 120°. This block is broken up and sieved and the pellets between 14 and 40 mesh are ignited at about 800° for 2 h.

Combustion tube packing

A roll of silver gauze (B.D.H. Microanalytical reagent, 30–60 mesh) of length 7 cm is placed in the beak end of the combustion tube with a few twisted strands of silver wire projecting into the exit tube. A loose plug of silica wool (1 cm long) is then inserted and is followed by a 10-cm layer of magnesium oxide pellets. This layer is compacted by gentle tapping and is held in position by another 1-cm plug of silica wool. The combustion tube is placed in the furnace so that the magnesium oxide layer lies centrally in the furnace; otherwise, the magnesium oxide may not be heated uniformly, owing to the temperature gradient of the furnace, and results will probably be low.

Magnesium oxide usually absorbs water at room temperature. After the apparatus has been set up, this is removed by passing a rapid flow of oxygen through the tube with the furnace at working temperature and with strong Bunsen heating at the forward end of the tube. The apparatus is then ready for use.

Procedure

The absorption tubes are wiped thoroughly in the conventional way and counterpoised at the beginning of each day while the furnace is heating to the working temperature. The tubes are then handled with gloves and only the ends are cleaned between analyses.

When the furnace has reached the working temperature, the whole train is connected up, the oxygen flow is adjusted by the needle valve to 12 ml/min and 80–100 ml of oxygen is passed through the apparatus. The absorption tubes are then disconnected and the ends are cleaned. The water absorption tube is weighed on the 7th min after removal from the train and the carbon dioxide absorption tube is weighed on the 11th min.

The sample (3–6 mg) is weighed in a platinum boat or a capillary in the usual way and is introduced into the combustion tube to a position 3–4 cm from the furnace after the absorption tubes have been replaced in the train. Volatile liquids should be placed farther from the furnace and a little more time should be taken for their volatilization. The sample is volatilized into the furnace with a low Bunsen flame during 7 min and then the tube around the sample container up to the furnace is heated strongly for 4 min. This is followed by a sweeping period of 5 min, during which the next sample can be weighed; the absorption tubes are then disconnected and weighed as before.

RESULTS

Results on a selection of standard and research compounds are shown in Table I. The errors are within the normally accepted limits for microanalysis. Fully fluorinated compounds and chlorofluorocarbons may give low results unless the combustion is done in moist oxygen. For such materials, a platinum boat containing a very little water is placed beyond the side-arm of the combustion tube after the sample has been introduced[1]. Fluorinated polymers can be analysed without difficulty.

TABLE I

Compound	*% Found*		*% Theoretical*	
	Carbon	*Hydrogen*	*Carbon*	*Hydrogen*
Trifluoromethylbenzoic acid (8 results)	50.57 ± 0.25	2.66 ± 0.2	50.54	2.65
Trifluoroacetanilide (8 results)	50.82 ± 0.28	3.23 ± 0.24	50.80	3.20
Perfluorosuccinic acid, aniline salt	51.02	4.10	51.06	4.26
Perfluoronaphthalene[a]	44.35	—	44.12	—
Perfluorodiphenyl[a]	43.43	—	43.11	—
Perfluoro-*p*-xylene[a]	33.81	—	33.57	—
Perfluoro-1,4-dimethylcyclohexane	23.86	—	24.00	—
3,3,4,4,5,5-Hexafluoropyran	31.06	2.43	30.93	2.06
1,2-Bis(trifluoromethyl)-3,5,6-trifluorophenyl-methyl sulphide	34.50	1.22	34.50	0.96
$C_{12}F_{21}Cl$	24.58	—	24.89	—
2,4,5,6-Tetrafluoro-3-aminohydrazine	37.08	2.59	36.97	2.56
1-Amino-3-iminoheptafluorocyclohexene	30.52	1.33	30.51	1.27
$CF_3 \cdot C_6H_4N(C_2H_5) \cdot SO_2C_6H_4 \cdot CH_3$	55.95	4.64	55.98	4.66
$CF_3C_6H_4P(C_2H_5)_2CdI_2$[b]	22.05	2.37	21.96	2.33
$[CF_3C_6H_4P(C_2H_5)_2]_2AgI$[b]	37.48	3.89	37.55	3.98
Anthracene	94.01	5.74	94.34	5.66
Naphthalene	93.50	6.24	93.71	6.29
Triphenylphosphine[b]	82.24	5.83	82.42	5.77

[a] Water (about 5 mg) added at side-arm where oxygen enters combustion tube.
[b] Sample covered with tungstic oxide and a second boat containing tungstic oxide introduced in front of sample boat.

The only compound so far encountered which did not decompose completely under the recommended conditions was perfluoroperhydropyrene[12], in which the carbon ring structure is wholly sealed off by fluorine atoms. However, correct and reproducible results were obtained when the temperature was increased to 950°. The difficulty encountered with this most unusual compound scarcely justifies a recommendation always to use a temperature of 950°, for analogous naphthalene and anthracene compounds decomposed readily at 850°.

For compounds containing phosphorus, the sample is covered with tungstic oxide and a porcelain boat containing tungstic oxide is placed half into the combustion furnace[13]; the analysis is then carried out in the normal manner. A covering of tungstic oxide is also used for alkali metal compounds[14].

Compounds containing no fluorine also give satisfactory results.

Simultaneous determinations on a series of research samples by the "slow" magnesium oxide method and the "rapid" one have given essentially the same results although the rapid method required only half the time. The series tested consisted of compounds containing about 15% to 70% of fluorine and varying from very stable solids to highly volatile liquids.

DISCUSSION

The success of this method for compounds containing much fluorine can readily be explained: since magnesium forms a very stable compound with fluorine, it would be expected that the remaining part of the molecule would break down as the fluorine is removed. Certainly little difficulty has been found in the decomposition of very stable, highly fluorinated substances even when they contain complicated ring structures or long chains. The satisfactory results obtained with compounds containing little or no fluorine are more difficult to explain, for magnesium oxide itself has no oxidising properties. Of course, entirely satisfactory carbon and hydrogen values can be obtained in a conventional tube with no packing at all provided that the temperature is high and the excess of oxygen large, and provided that a careful volatilization technique is employed[15]. The magnesium oxide in the present method may simply act as a plug in the tube to prevent a too rapid progress of the volatilising sample through the hot combustion zone, or some contact catalytic action may play a part; probably both modes of action contribute to the success of the method. In any case, it is interesting to note that moderate "flashing" of the sample during volatilization has less effect on the results than it has in the analogous "slow" methods.

The high temperature used is vital. Naphthalene, for example, is only slightly decomposed at a temperature of 600°, although it is completely converted to carbon dioxide and water at 800°. Moreover, since magnesium oxide retains carbon dioxide up to about 700° it is important to check that all the magnesium oxide layer is at the correct temperature of 820–850°. The normal temperature gradient of the furnace ensures that the silver gauze does not become over-heated.

For convenient usage in routine work, the type of magnesium oxide is important. In initial tests "light" magnesium oxide was used to make the pellets for the tube filling. These pellets were hard and very satisfactory from the point of view of analytical results, but they shrank during the course of about 10 analyses to about half their original bulk, probably because of gradual conversion to a denser form. Thus the tube filling had to be checked each day and replenished; this could be done readily when the absorption tubes were repacked. However, other forms of magnesium oxide were examined to see if the inconvenience of constant replenishment could be avoided. "Heavy" magnesium oxide did not pellet so well as the "light" form and tended to powder in the tube. A 3 : 1 mixture of "heavy" and "light" grades of normal pharmaceutical quality gave quite hard pellets which had only a small tendency to shrink. Analytical reagent grade magnesium oxide was not examined, since the above mixture, which is very much cheaper, proved satisfactory.

Generally, 60–70 analyses can be done on the same filling, but it may be necessary to tamp the filling gently after about 30 analyses. Repacking the combustion tube is extremely simple since no conditioning is needed before satisfactory results can be obtained. One combustion tube of top grade silica should be usable for about 200 analyses.

Although no compound has yet been encountered which fails to give correct results, or to give results similar to those obtained by other combustion methods, we prefer to recommend this procedure only for fluorinated materials. For unfluorinated substances, the cobalto-cobaltic oxide method of VEČEŘA[9] is more efficient in that the temperature required is only 600° and the time required for combustion and sweeping

is only 10 min. However, this method is not satisfactory for highly fluorinated materials[10]. It should, of course, be possible to develop a "universal" packing based on cobalto-cobaltic oxide, magnesium oxide and silver, but in so doing, the simplicity, speed and economy of the separate methods would be lost.

ACKNOWLEDGEMENTS

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SUMMARY

A rapid determination of carbon and hydrogen in organic fluorine compounds is described. Magnesium oxide is used both as an absorbent for fluorine and as an aid to complete combustion. The time required for one determination in series is under 30 min. The method is very widely applicable.

RÉSUMÉ

Une méthode est décrite pour le dosage rapide du carbone et de l'hydrogène dans des substances organiques fluorées. L'oxyde de magnésium utilisé permet à la fois d'absorber le fluor et de faciliter la combustion.

ZUSAMMENFASSUNG

Beschreibung einer Schnellmethode zur Bestimmung von Kohlenstoff und Wasserstoff in organischen Fluorverbindungen. Die Füllung des Verbrennungsrohres besteht lediglich aus Magnesiumoxyd und Silber. Die Beleg-Analysen zeigen die Brauchbarkeit dieser Rohrfüllung auch bei fluorfreien Verbindungen.

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DETERMINATION OF SOLUBLE AND INSOLUBLE ZIRCONIUM IN MAGNESIUM ALLOYS

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When magnesium–0.5% zirconium alloys are dissolved in dilute acids, a complete solution is normally obtained, but sometimes a considerable amount of a black insoluble material separates, which chemical examination shows to be mainly zirconium. This has been shown[1] to be due to the presence in the alloy of a second phase. X-Ray examination has shown that this insoluble fraction is mainly zirconium hydride[2]. We have found that the appearance of this insoluble zirconium fraction does in fact usually coincide with a considerable increase in the hydrogen content of the material, as shown in Table I. The maximum hydrogen content, if all the hydrogen were

TABLE I

Zirconium (%)		*Total hydrogen (p.p.m.)*
Soluble	*Insoluble*	
0.45	0.02	5, 13, 13
0.45	Nil	5, 7
0.43	0.06	8
0.50	0.02	4
0.52	0.03	10, 13
0.36	0.08	27
0.02	0.37	39, 54, 31, 50
0.06	0.50	23, 24, 56, 41
0.02	0.60	60

converted to $ZrH_{1.55}$, would be about 80–90 p.p.m. The hydrogen content was determined by an oxidation method, where the sample is burnt at 800° in an oxygen/argon mixture and the evolved water is measured manometrically. (Another method for determination of hydrogen, where the magnesium alloy is heated in vacuum at 450° and the evolved hydrogen is measured, was found to be unsatisfactory, presumably because at this temperature the zirconium hydride did not break down. At higher temperatures, magnesium volatilised and spurious results were obtained, due to the reaction of the magnesium with water films on the apparatus).

Methods of analysis for the determination of zirconium in magnesium–zirconium alloys have been described[3–6]. In the alizarin red S absorptiometric method[3,4] the alloy is dissolved in acid and zirconium is complexed directly with alizarin red S. If

insoluble zirconium is present, this can be filtered on a pulp pad, the zirconium on the pad brought into solution (after ignition) by treatment with hydrofluoric acid, and determined separately. PAPUCCI AND KLINGENBERG[5] use *p*-bromo- or *p*-chloromandelic acid in a gravimetric procedure; this is satisfactory, but is somewhat tedious and the reagent is expensive. Another procedure[6] has been investigated, but magnesium appeared to interfere. This may be due to the origin of the neothoron used, but this was not examined further. We have used the alizarin red S method[3] with a varying degree of success. It is possible to lose some of the soluble zirconium by absorption on the paper pulp, so obtaining a low figure for the soluble zirconium. When hydrofluoric acid is used to dissolve the insoluble zirconium from the pad, it is difficult subsequently completely to eliminate the excess fluoride — even μg quantities of residual fluoride cause low figures for the insoluble zirconium. Because of these difficulties, we investigated a procedure described by YOUNG AND WHITE[7] for the determination of zirconium. In this method a solvent extraction procedure is used to remove zirconium from interfering metals; trioctyl phosphine oxide in cyclohexane extracts zirconium from 7 *N* hydrochloric acid solution. Zirconium is subsequently determined in the organic phase with pyrocatechol violet as reagent. The reagent is about 5 times as sensitive as alizarin red S (molecular absorption $\sim$ 33,000 at 640 mμ, against 5,500 at 525 mμ for alizarin red S). Under the conditions described only titanium would interfere, and this is normally less than 0.01% in the alloys concerned. This method is reproducible in the presence of large amounts of magnesium and gives excellent recoveries on synthetic samples containing also iron, zinc, cerium and rare earths, and aluminium.

When insoluble zirconium is present, we have found that if the alloy is dissolved in dilute hydrochloric acid, and the normal procedure is adopted, one obtains a figure for zirconium which corresponds to that of the "soluble" fraction only, *i.e.* the insoluble zirconium remains in suspension in the aqueous phase and is not extracted by the trioctyl phosphine oxide. If, however, the insoluble zirconium is brought into solution by the addition of a very small amount of hydrofluoric acid, the excess complexed with boric acid and the usual procedure is then followed, one obtains a figure for soluble and insoluble zirconium (total zirconium). The amount of hydrofluoric acid present should not exceed 0.5 ml of 5% HF. (Larger amounts of hydrofluoric acid give low figures). Since 0.1 ml of 5% hydrofluoric acid is adequate to dissolve up to 0.5% "insoluble" zirconium in an 0.2-g sample (aliquot $\equiv$ 0.01 ml 5% hydrofluoric acid), interference is negligible under the conditions described later.

It is possible to determine soluble and total zirconium (insoluble by difference) on the same solution. The alloy is dissolved in dilute acid and the solution diluted to a known volume. Two aliquots are taken for the soluble zirconium, then two further aliquots are taken for the total zirconium. This could lead to error however if the insoluble zirconium did not remain in perfect suspension, so it is recommended that two separate samples be taken for soluble and total zirconium determination.

PAN as reagent

After the experiments described above had been completed our attention was drawn to a method described by ROLF[8] where zirconium is separated by an extraction procedure using dibutyl phosphoric acid and then determined in the organic phase using pyridyl-azo-naphthol (PAN) as reagent. In view of the instability of the

pyrocatechol violet reagent (necessitating rapid measurement of the absorption at high zirconium concentrations) this alternative reagent for zirconium was investigated. It was found that PAN could be substituted for pyrocatechol violet in the procedure already being used, to give a much more stable complex. The absorption of the complex increased slightly up to 15 min, and was then stable for at least 2 days. It was also found that 2 ml of aniline could be substituted for pyridine (used as buffer) without affecting the absorption. Experiments were carried out to ascertain the interference by fluoride, aluminium, zinc, cerium and iron; there was no interference from less than 1 ml of 5% hydrofluoric acid, or from less than 2% of the metals.

The reagent sensitivity at 550 mμ was approximately the same as that of pyrocatechol violet at 640 mμ.

EXPERIMENTAL

Reagents

(*a*) *0.4% Trioctyl phosphine oxide* (Kodak) in cyclohexane or 100°–201° petroleum ether.

(*b*) *0.05% Pyridyl-azo-naphthol (PAN)* in A.R. methanol (stable for at least 2 weeks).

(*c*) *Aniline* (A.R.). A discoloured reagent will give a high blank figure and should be redistilled before use.

5% Hydrofluoric acid in a polythene dropping bottle.

All other reagents were of analytical reagent grade.

Standard zirconium solution (1 ml $\equiv$ 1 mg zirconium). Dissolve 0.25 g of high purity zirconium in 5 ml of hydrofluoric acid and 30 ml of water in a platinum dish. Add 20 ml of perchloric acid and evaporate to heavy fumes. Cool, rinse the walls of the dish with a little water, add a further 10 ml of perchloric acid and again evaporate to fumes. Cool. Extract with 50 ml of 20% hydrochloric acid and dilute to 250 ml. Dilute 5 ml to 250 ml with 2% hydrochloric acid to give a solution of which 1 ml $\equiv$ 20 μg zirconium.

Procedure

A. Total zirconium. Dissolve 0.2 g of alloy in 4 ml of water and 2 ml of hydrochloric acid added dropwise. Heat on a water bath for 5 min, cool, and add 2 drops (*ca.* 0.1 ml) 5% hydrofluoric acid to dissolve any insoluble zirconium. Dilute to 100 ml. Transfer a 10-ml aliquot to a 75-ml separating funnel, add 15 ml of hydrochloric acid and 1 g of ammonium thiocyanate and shake to dissolve. Add 0.5 g of boric acid and again shake to dissolve. By pipette add 5 ml of trioctyl phosphine oxide solution, and shake vigorously for at least 2 min. Run off the aqueous layer and reject. Take a 3-ml aliquot of the organic layer in a dry pipette and transfer to a dry 25-ml graduated flask. Add 10 ml of methanol, and 2 ml of 0.05% PAN solution. Mix well, add 2 ml of aniline and dilute to 25 ml with methanol. Leave for 15 min. Measure the absorption at 550 mμ, using 1-cm cells for the range 0–0.5% or 0.5-cm cells for the range 0.5–1.0%. (This range can be extended to 3% if a 1-ml aliquot of the organic layer is taken).

B. "Soluble" zirconium. The above procedure is repeated, omitting the hydrofluoric acid.

Calibration: Take 0, 1, 2, 3, 4, 5, 6, 8, 10 ml of the dilute standard zirconium solution, dilute each to 10 ml, add 15 ml of hydrochloric acid, etc. and proceed as above. It is advisable to check one point when a fresh batch of PAN reagent is used.

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SUMMARY

A method for the determination of soluble and insoluble zirconium is described. To differentiate between the two forms, two solutions are prepared, in one of which the insoluble zirconium remains in suspension; in the other it is brought into solution with hydrofluoric acid. Zirconium is extracted by trioctyl phosphine oxide/petroleum ether and determined in the extract spectrophotometrically with pyridyl-azo-naphthol (PAN) as reagent.

RÉSUMÉ

Une méthode est proposée pour le dosage du zirconium (soluble et insoluble) dans des alliages de magnésium. On prépare deux solutions: Dans l'une le zirconium insoluble reste en suspension, dans l'autre on ajoute de l'acide fluorhydrique pour le dissoudre. Le zirconium est extrait par le mélange oxyde de tri-octylphosphine/éther de pétrole et dosé spectrophotométriquement au moyen de pyridylazonaphtol.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von löslichem und unlöslichem Zirkonium in Magnesiumlegierungen. In einer Probe bestimmt man den gelösten Anteil von Zirkonium durch Extraktion mit Trioctylphosphinoxyd. In einer zweiten Probe bringt man das unlösliche Zirkonium durch Zusatz von Fluorwasserstoffsäure in Lösung und extrahiert wie bei der ersten Probe; man erhält hierbei die Gesamtmenge an Zirkonium. Die beiden Extrakte werden nach Zusatz von Pyridylazonaphtol (PAN) spektrophotometrisch gemessen. Die Differenz beider Messungen ergibt den Gehalt an unlöslichem Zirkonium.

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CHLORPROMAZINE HYDROCHLORIDE AS AN ANALYTICAL REAGENT

PART I. SPOT TESTS FOR INORGANIC IONS

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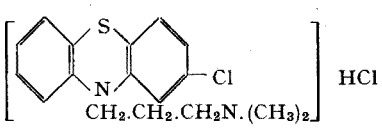
Chlorpromazine hydrochloride is an important tranquilizing agent which has the following chemical structure:



The sulphur atom in this molecule is very susceptible to oxidation. The oxidation product which has been designated as a free radical from its electronic spin[1] and titrimetric evidence[2] is red in colour having an absorption maximum at 530 mμ (Fig. 1). MICHAELIS, GRANICK AND SCHUBERT have studied methylene blue and other phenothiazine derivatives which also yielded free radicals on oxidation[3-5].

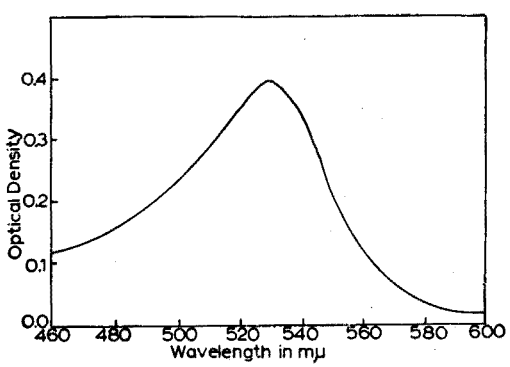


Fig. 1. Spectra of oxidized chlorpromazine hydrochloride in 20% phosphoric acid.

The red coloured free radical is stable in acid media. MICHAELIS *et al.* attributed the stability of this type of free radical to the formation of a bivalent cation which exhibits equivalent resonance of the same type as a Wurster radical. These authors

also showed that the S-bridge makes possible a particular kind of resonance which acts as a stabilising factor. Several methods of determination of chlorpromazine hydrochloride and its related compounds in biological fluids are based on the estimation of the red colour formed when these compounds react with various oxidizing agents[6-9].

Phenothiazine also reacts with certain metals to form complexes[10,11]. RYAN[12] and CAVATORTA[13] used palladium chloride as the complexing agent for the determination of chlorpromazine hydrochloride in pharmaceutical preparations.

Although several papers have been published on methods of identification and determination of chlorpromazine hydrochloride and other N-substituted phenothiazine derivatives such as promazine, promathezine and perchlorperazine maleate etc., their uses as analytical reagents have never been studied in any detail. Among the phenothiazine derivatives thus far studied in this laboratory the propyl dimethylamine-linked ones are most versatile for analytical purposes. They are stable, water-soluble and very reactive compounds. In solution they are colourless which is a great asset for colorimetric determinations. Investigations have shown that the reducing and complexing properties of chlorpromazine hydrochloride can be used for the detection and quantitative determination of several inorganic ions. A short series of papers will be published on its uses as an analytical reagent and the present paper discusses the use of chlorpromazine hydrochloride for the detection of micro quantities of gold, cerium, iron, chromate, permanganate, bromate, iodate, bromide, iodide, nitrite, platinum and palladium.

EXPERIMENTAL

Reagent

Aqueous chlorpromazine hydrochloride solution, 25 mg/ml.

General procedure for the detection of some oxidizing agents

A drop of the test solution is mixed with a drop of *N* hydrochloric acid followed by a drop of chlorpromazine hydrochloride solution in a spot plate. A red colour that appears immediately after the addition of the chlorpromazine hydrochloride indicates the presence of an oxidizing agent. The detection limits are as follows:

Ion	Au^{+3}	Ce^{+4}	Fe^{+3}	$Cr_2O_7^{-2}$	MnO_4^-	BrO_3^-	IO_3^-	NO_2^-
μg	0.05	0.02	8.0	0.05	0.05	0.2	0.2	0.004

Detection of palladium and platinum

Single drops of the test solution, *N* hydrochloric acid and chlorpromazine hydrochloride solution are mixed in a spot plate. If palladium is present an orange red coloration appears. With chloroplatinic acid the colour changes from red to violet and finally to blue.

Detection of platinum and palladium in the presence of oxidizing agents

The free radical produced by the oxidation of chlorpromazine hydrochloride is not extracted by chloroform but the complexes formed when palladium chloride and chloroplatinic acid react with chlorpromazine hydrochloride are soluble in chloroform. This forms a basis for the detection of platinum and palladium in the presence of oxidizing agents.

Procedure. A drop of the test solution is mixed with a drop of *N* hydrochloric acid and a drop of chlorpromazine hydrochloride solution in a micro test tube. After 5 min a drop of chloroform is added and the mixture is shaken. A blue colouration in the chloroform layer indicates the presence of platinum and a yellow colouration

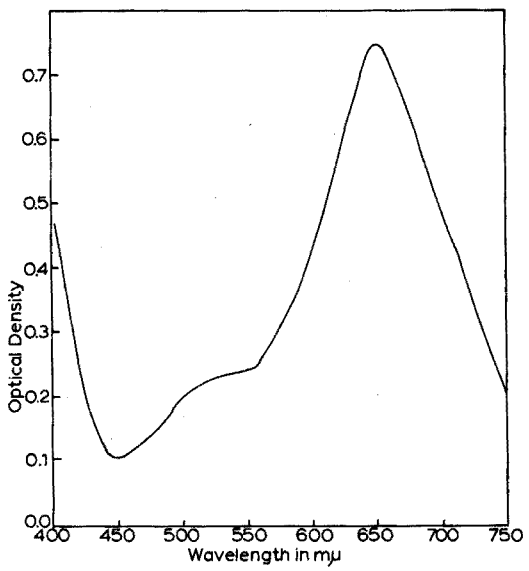


Fig. 2. Spectra of platinum–chlorpromazine hydrochloride complex in chloroform.

indicates the presence of palladium. The absorption spectra of these two complexes in chloroform are shown in Figs. 2 and 3. The limits of detection for both platinum and palladium are 5 μg.

Detection of gold(III) and cerium(IV) in presence of iron(III)

Large amounts of iron(III) interfere with the tests for gold(III) and cerium(IV) ions. However phosphoric acid complexes iron(III) and thus prevents its reaction with chlorpromazine hydrochloride.

Procedure. A drop of the sample and a drop of 20% phosphoric acid are placed on a spot plate followed by a drop of the chlorpromazine hydrochloride solution. When gold(III) or cerium(IV) is present an immediate red colour develops. The following ions interfere: Pt^{+4}, Pd^{+2}, $Cr_2O_7^{-2}$, MnO_4^-, BrO_3^-, and IO_3^-.

Detection of platinum in the presence of palladium

Both platinum and palladium form coloured complexes with chlorpromazine hydrochloride, hence palladium interferes with the detection of platinum. However, palladium reacts with dimethylglyoxime to form an inner complex, which masks the reaction with chlorpromazine hydrochloride, hence platinum can be detected in the presence of large amounts of palladium after addition of dimethylglyoxime.

Procedure. A drop of the test solution, a drop of *N* hydrochloric acid and a drop of

alcoholic 1% dimethylglyoxime solution are placed in a micro test tube, followed by a drop of chlorpromazine hydrochloride reagent. If platinum is present the solution attains a pinkish colouration which gradually turns to violet. When a drop of chloroform is added and shaken, the chloroform layer acquires a blue colour.

This procedure is specific for the detection of platinum since other oxidizing agents do not interfere.

Detection of bromides and iodides

Small quantities of bromides and iodides do not react with chlorpromazine hydrochloride. To carry out the test for bromides and iodides they must be oxidized to free bromine or iodine by treatment with chromic acid.

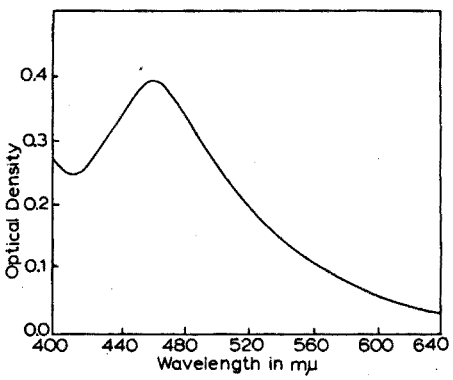


Fig. 3. Spectra of palladium–chlorpromazine hydrochloride complex in chloroform.

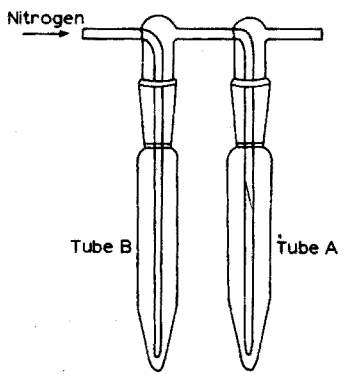


Fig. 4. Apparatus used for detection of bromine and iodine (tube diam. 2 cm; length 11 cm).

Procedure. The apparatus used is shown in Fig. 4. A few drops of hydrochloric acid and a few drops of chlorpromazine hydrochloride solution are placed in tube A of the apparatus. A drop of the test solution together with 1 ml of 60% chromic acid are placed in tube B. The apparatus is then closed and nitrogen gas is bubbled through the system at a rate of approximately 2 bubbles per sec. If bromides or iodides are present, the solution in tube A acquires a red colour after 5 to 10 min. The limit of detection for both bromide and iodide is 0.5 μg.

Interference of foreign ions

The following ions were found to give no red colour with chlorpromazine hydrochloride under the conditions described: Ag, Na, K, Ca, Ba, Sr, Co, Ni, Cd, Zn, Cu, Hg, As, Mn, Pb, Cr, Al, UO_2^{-2}, and ClO_3^-.

Since the development of the red colour depends on the oxidation of chlorpromazine hydrochloride, powerful reducing agents such as stannous chloride, titanous chloride, hydroquinone and ascorbic acid interfere.

CONCLUSION

Although chlorpromazine hydrochloride has been used for the detection of several ions, the tests can be made specific under certain conditions which are described under the

various sections. The test for bromide and iodide, for example, is particularly useful for the detection of these ions in articles damaged by sea water. The test described is as sensitive and specific as the eosin test described by SEABER[14]. Chlorides, and oxidizing, reducing, and complexing agents mentioned earlier do not interfere.

The reagent is also useful for the detection of nitrites in firearms, a routine procedure to establish whether the firearms have been recently fired. The sensitivity of the test is comparable to that using sulphanilic acid and naphthylamine. Phosphoric acid must be used to mask any iron(III) that may be present in the rinsings of the chambers or barrels of the firearms.

ACKNOWLEDGEMENT

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SUMMARY

Chlorpromazine hydrochloride is proposed as a spot test reagent for the detection of gold, cerium, iron, chromate, manganate, bromate, iodate, nitrite, bromide, iodide, platinum and palladium. Conditions for the suppression of certain interfering substances are also given.

RÉSUMÉ

Le chlorhydrate de chloropromazine est proposé comme réactif à la touche pour l'identification des éléments et ions suivants: or, cérium, fer, chromate, manganate, bromate, iodate, nitrite, bromure, iodure, platine et palladium. Des moyens d'éliminer certaines substances gènantes sont donnés.

ZUSAMMENFASSUNG

Das Chloropromazinhydrochlorid wird als Tüpfelreagenz zum Nachweis von Gold, Cerium, Eisen, Chromat, Manganat, Bromat, Iodat, Nitrit, Bromid, Iodid, Platin und Palladium vorgeschlagen. Die Ausschaltung des Einflusses störender Substanzen wird beschrieben.

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MASKING ACTION OF COMPLEXANS ON QUALITATIVE INORGANIC REACTIONS

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Although the analytical aspects of complexometric titration with the complexan EDTA are well known much less information is available on the masking action of EDTA in qualitative inorganic reactions and apart from CDTA (1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid) few of the other complexans are employed in qualitative or quantitative work. PŘIBIL[1] has presented a useful survey of the masking actions of EDTA in qualitative inorganic analysis and whilst this manuscript was in preparation a considerably more detailed account of similar experiments on the masking action of EDTA has been given by CHENG[2]. The stability constants of many metal-complexan chelates are available[3], but these at best can only serve as a rough guide to the potential applications of these reagents as masking agents. The influence of pH, the presence of precipitating species and other complex forming ions, etc.,

TABLE I

Standard abbreviation	*Complexan*	*Standard abbreviation*	*Complexan*
EDTA	Ethylenediamine tetraacetic acid	EDDA	Ethylenediamine-N,N′-diacetic acid
MEDTA	1,2-Propylenediamine tetraacetic acid	UDA	Uramildiacetic acid
2:3-BDTA	2,3-Butylenediamine tetraacetic acid	NTA	Nitrilotriacetic acid
DTPA	Diethylenetriamine pentaacetic acid	MIDA	N-Methyliminodiacetic acid
DPTA	1,3-Propylenediamine-2-ol-tetra-acetic acid	IDA	Iminodiacetic acid
CPDTA	1,2-Diaminocyclopentane tetra-acetic acid	DHEG	Di-(2-hydroxyethyl)glycine
CDTA	1,2-Diaminocyclohexane tetraacetic acid	AADA	Anthranilic acid diacetic acid
MCDTA	4-Methyl-1,2-diaminocyclohexane tetraacetic acid	CHEL ME	2,2′-Bis[di(carboxymethyl)amino] diethyl ether
CHDTA	1,2-Diaminocycloheptane tetra-acetic acid	EGTA	1,2-Bis [2-di(carboxymethyl) aminoethoxy] ethane
		HEED-TA	N-hydroxyethyl ethylenediamine-N,N′N′-triacetic acid
		CHEL 138	NN′-Ethylene-bis [2-*o*-hydroxy-phenyl)] glycine

have a pronounced effect on the position of equilibrium in a chemical system. For example EDTA forms a considerably more stable chelate with zinc ($^{10}\log K = 16.1$) than with calcium ($^{10}\log K = 10.6$) so that zinc can be titrated in the presence of calcium in acid solution when the weaker chelate is dissociated. On the other hand in an alkaline medium, the situation is reversed and calcium is titrated completely before attack begins on the zinc ion which is now complexed by oxygen as the zincate ion[4].

In the present paper we report the influence of 20 complexans on a variety of standard inorganic reactions most of which are used in qualitative inorganic analysis. The complexans are listed in Table I. Most of them are commercially available; the synthesis of others has recently been described in the literature[5].

The tests described below are arranged according to the chemical grouping of the cations within classical qualitative analytical schemes. In addition, for ease of reference, a summary of information is presented in Tables II–V. This should *only* be used in conjunction with the text.

RESULTS

The various tests described below were carried out with 0.02 *M* solutions and, unless otherwise mentioned, with a one-fold excess of complexan added to test the masking action.

TABLE II

REACTIONS OF THE CHLORIDE-GROUP METALS

Cation	*Ag⁺*						*Pb⁺²*		*Tl⁺*				
Anion or reagent	*Cl⁻*	*Br⁻*	*I⁻*	*CrO_4^{-2}*	*MoO_4^{-2}*	*WO_4^{-2}*	*WO_4^{-2}*	*MoO_4^{-2}*	*I⁻*	*I⁻*	*CrO_4^{-2}*		*CNS⁻*
pH[a] Medium	*LN*	*LNH*	*LNH*	*4.3 HAc⁻*	*N*	*N*	*6*	*6*	*H NH_3*	*L*	*L HAc⁻*	*H NH_3*	*N*
Complexan													
DHEG	—	—	—				±	±		—	—		
IDA	—	—	—				±	±		—	—		
MIDA	—	—	—				±	±		—	—		
UDA	—	—	—				±	±		—	—		
EDDA	—	—	—				±	±		—	—		
AADA	—	—	—				+	—		—	—		
NTA	—	—	—	—	±	+	+	—	±	—	—	±	—
CHEL 138	—	—	—							—	—		
CHEL ME	—	—	—				+	±		—	—		
EGTA	—	—	—				+	—		—	—		
HEEDTA	—	—	—				+	+		—	—		
EDTA	—	—	—	+	+	+	+	+	+	—	—	+	—
MEDTA	—	—	—	±	+	+	+	+	+	—	—	+	—
2:3-BDTA	—	—	—	+	+	+	+	+		—	—		
DPTA	—	—	—	+	+	+	+	+	—	—	—	+	±
DTPA	—	—	—	+	+	+	+	+	—	—	—	+	—
CPDTA	—	—	—	—	±	±	+	+	+	—	—	+	—
CDTA	—	—	—	+	+	+	+	+	+	—	—	+	±
MCDTA	—	—	—		+	+				—	+	+	
CHDTA	—	—	—	+	+	+	+	+	+	—	—	+	±

[a] L = low, N = neutral, H = high

Key: + reaction masked; — reaction not masked; ± incomplete masking or indeterminate reaction

(A) *The chloride group metals*

Silver

None of the complexans will prevent the precipitation of the silver halides in neutral or acid solution nor of the bromide and iodide in alkaline solution, but the precipitation of silver chromate using 0.02 *M* solutions from an acetic acid buffer, pH 4.3, is prevented by an excess of EDTA (as reported previously by PŘIBIL[1]) and also by DTPA, DPTA, MEDTA, CDTA, CHDTA, 2:3-BDTA, but not by the weaker complexans, *e.g.* NTA.

All the complexans in column I of the Table prevent the precipitation of silver tungstate and molybdate in neutral solution though the action of CPDTA is rather indeterminate in both cases.

Lead

The precipitation of lead as chromate in acetic acid solution is prevented by most of the complexans. Most of them also mask precipitation of lead tungstate at pH 6 except IDA, MIDA, EDDA, UDA and DHEG which give incomplete masking. In the study of lead molybdate, EGTA, AADA and NTA do not prevent precipitation, IDA, MIDA, EDDA, CHEL ME, UDA and DHEG give partial masking and EDTA, MEDTA, 2:3-BDTA, DPTA, DTPA, HEEDTA, CPDTA, CDTA and CHDTA prevent precipitation at pH 6.

Mercury(I)

The reactions of mercury(I) were not pursued because of the more or less immediate black precipitate which is obtained following the addition of a complexan to a mercury(I) solution.

Thallium(I)

The precipitation of thallium(I) as chloride is not prevented by complexan in weakly acid solution and as noted by PŘIBIL[1] thallium iodide is prevented from precipitation by EDTA in ammoniacal solution. In addition, CPDTA, CDTA, CHDTA and MEDTA also mask thallium iodide but DPTA and DTPA appear to allow full precipitation. NTA allows partial precipitation. No complexan prevents precipitation in acid solution.

Only MCDTA is found to mask the precipitation of thallium(I) chromate from acetic acid solution. In ammonia all the complexans in column I prevent precipitation; NTA gives only incomplete masking. In neutral solution partial masking of the precipitation of thallium thiocyanate is observed with DPTA, CDTA and CHDTA; no masking takes place with the others.

(B) *Acid sulphide group*

Copper(II)

All the complexans in column I prevent the reaction between Cu(II) and iodide or thiocyanate except that in the latter instance the masking by CPDTA, as with weaker reagents such as NTA, is incomplete. With copper(I) only CDTA is effective in preventing the precipitation of cuprous thiocyanate; EDTA, CPDTA, DPTA, and NTA exert no apparent masking action and DTPA, MEDTA and CHDTA are only partially effective. In an acetic acid medium all the column I complexans held up

copper(II) sulphide temporarily though EDTA and CHDTA appear to be the most effective; weak complexans such as NTA do not prevent precipitation. In an ammoniacal medium, the action of sulphide on copper(II) is masked only by CDTA and CHDTA; partial masking is observed with MEDTA and DTPA. The precipitation of copper(II) ferrocyanide in weakly acid solution (pH 5) is prevented by EDTA, CPDTA, CDTA, MCDTA and CHDTA; IDA, EDDA, UDA and DHEG are ineffective.

Cadmium

The precipitation of cadmium sulphide from near neutral solution is masked only by CHDTA and CDTA. In the former instance precipitation may take place on standing for a short time. All the complexans in column I mask the well known Cadion test, but it proceeds normally in the presence of weaker complexans such as NTA.

Mercury(II)

None of the complexans prevents the reduction of mercury(II) by tin(II) chloride. In neutral solution, the precipitation of red mercury(II) iodide is prevented by CDTA, CHDTA, MEDTA and DPTA; partial masking occurs with EDTA whilst CPDTA, DTPA and NTA are ineffective.

TABLE III

REACTIONS OF THE SULPHIDE-GROUP METALS

Cation	Cu^{+}	Cu^{+2}					Cd^{+2}		Hg^{+2}	Co^{+2}	Ni^{+2}			Zn^{+2}		Mn^{+2}	Bi^{+3}		Sn^{+4}
Anion or reagent	CNS^-	I^-	CNS^-	S^{-2}	$Fe(CN)_6^{-4}$	5	S^{-2}	*Cadion*	Sn^{+2}	I^-	S^{-2}	S^{-2}	*DMG*	S^{-2}	$Fe(CN)_6^{-4}$	S^{-2}	S^{-2}	OH^-	S^{-2}
pH[a]	N	N	N	L	H		N			N	H	H	H	H	H		10	L	H	L
Medium				*HAc*	NH_3						NH_3	NH_3	NH_3	NH_3	NH_3		NH_3	*HCl*	NH_3	*HCl*
Complexan																				
DHEG						—							—		—					
IDA						—							—		—					
MIDA													—		—					
UDA						—							—		—					
EDDA						—							—		—					
AADA													—		—					
NTA	—		±	—	—		—	—	—	—	±		—	—	—	+	—	—	—	
CHEL 138															—					
CHEL ME													—							
EGTA													—							
HEEDTA													+					—	+	—
EDTA	—	+	+	+	—	+	—	+	—	±	+	+	+	+	+	+	—	+	+	
MEDTA	±	+	+	±	±		—	+	—	+	+	+	+	+		+	—	+	+	
2:3-BDTA														+		+				
DPTA	—	+	+	±	—		—	+	—	+	+	+	+	+		+	—	+	±	
DTPA	±	+	+	±	±		—	±	—	—	+	+	+	+		+	—	+	±	
CPDTA	—	+	±	±	—	+	—	+	—	—	+	+	+	+	+	+	—	+	+	
CDTA	+	+	+	±	+	+	+	+	—	+	+	+	+	+	+	+	±	+	+	
MCDTA		+	+	±		+	—	+						+	+	+				
CHDTA	±	+	+	+	+	+	+	+	—	+	+	+	+	+	+	+	±	+	+	

[a] L = low, N = neutral, H = high

Key: See Table II

Bismuth

The precipitation of bismuth sulphide from hydrochloric acid solution is not prevented by EDTA, MEDTA, HEEDTA, DPTA, CPDTA or NTA and the weak complexans. Slow precipitation occurs with DTPA whilst with CDTA and CHDTA the precipitate only appears on standing for some time. All the complexans mentioned above prevent the precipitation of basic bismuth salts upon addition of ammonia to the solution, but the masking by NTA is incomplete.

Tin(IV)

The precipitation of tin(IV) sulphide in a hydrochloric acid medium is prevented by EDTA, CPDTA, CDTA and CHDTA. Normal precipitation appears to occur in the presence of NTA and HEEDTA. Partial precipitation occurs with DPTA and DTPA.

(C) *The hydroxide group*

Iron(III)

The formation of a wine-red complex with thioglycollic acid is prevented by the previous addition of CDTA and CHDTA to an iron(III) solution followed by thioglycollic acid (dilute) and pH 10 ammonia buffer.

Masking is also possible with MEDTA, EDTA and 2:3-BDTA when the solution is allowed to stand before addition of thioglycollic acid. Partial masking occurs with CPDTA, DPTA, DTPA and HEEDTA; no masking is observed with NTA, but variable results may be obtained depending on the excess of reagent and complexan used. All the column I complexans prevent the colour reaction with 7-iodo-8-hydroxyquinoline-5-sulphonic acid (Ferron) but NTA does not. The iron(III) ferrocyanide reaction is prevented by MEDTA, CPDTA, CDTA and CHDTA whilst EDTA causes partial masking; DPTA, DTPA and NTA are ineffective. The colour reaction between iron(II) and dimethylglyoxime in ammoniacal solution is masked by EDTA, MEDTA, CPDTA, CDTA and CHDTA, but not by DPTA and NTA. Only CHDTA appears to suppress the reaction of iron(II) with *o*-phenanthroline in an acetate buffer.

One of the most interesting reactions of the complexans in these masking procedures occurs when attempts are made to mask the precipitation of iron(III) by sulphide, in an ammoniacal medium. PŘIBIL[1] reports that an excess of ammonium sulphide does not bring down the sulphide from iron(III)–EDTA; with sodium sulphide, a precipitate appears, but it is of a colloidal nature and cannot be readily filtered or centrifuged. Our early experiments using very large excesses of sodium sulphide were such that we obtained an immediate black precipitate on adding sodium sulphide to a neutral or alkaline solution of iron(III) containing excess of EDTA. No precipitate was formed when CPDTA, CDTA, MCDTA and CHDTA were used, though precipitation did occur shortly afterwards with CPDTA and CDTA. Subsequently, however, the use of a less highly concentrated sodium sulphide solution (*ca.* 1%) gave vastly different results. Thus with EDTA, CPDTA, CDTA, MEDTA and CHDTA red-pink soluble complexes are obtained upon addition of sodium sulphide to the iron(III) solution containing excess of complexan and ammonia. These colours slowly fade through colourless to dark green. With NTA however and most of the weak complexans a green colour is formed immediately which in some cases (*e.g.* NTA) deepens rapidly to form a very intense colour. The very weak com-

plexans, IDA, MIDA, EDDA, yield precipitates as well as the green colour. It is not clear whether this colour is due to colloidal iron(III) sulphide, although the conditions of formation are such that one would expect the complexan-controlled concentration of free iron(III) ions to result in slow formation of iron(III) sulphide and, consequently, dense granular precipitates. A quantitative study of this reaction reveals that it may be used selectively for the colorimetric determination of iron(III) or (over a limited range) sulphide ion[6]. Iron(II) appears not to furnish this reaction except by oxidation to iron(III). This valency transformation occurs very readily in the presence of complexans.

Aluminium

The precipitation of aluminium hydroxide is readily masked by the strong complexans such as EDTA, CPDTA, CDTA, MCDTA, as is the colour reaction between alizarin and aluminium in an ammoniacal solution. On the other hand NTA does not prevent this latter reaction; DPTA causes only partial masking.

Chromium

Chromium(III) reacts only slowly with EDTA and when ammonia and phosphate are added, it is possible to obtain a normal test for chromium(III) if the reagent is added soon after the complexan (even with the strongest complexans). If, however, the solution containing the chromium(III) and complexan is boiled the precipitation of chromium(III) hydroxide is prevented by EDTA, DPTA, DTPA, CPDTA, CDTA, CHDTA but not by NTA. MEDTA, HEEDTA and CHDTA show a pronounced tendency to precipitate the chromium.

Titanium

None of the complexans examined masks the ammonia precipitation of titanium nor the colour formation with hydrogen peroxide at pH 1. In near neutral solution however, CDTA, MCDTA and CHDTA seem to be effective in masking the latter reaction.

None of the complexans prevents precipitation of titanium cupferrate or the titanium-N-benzoylphenylhydroxylamine compound, but in the latter instance a combination of peroxide and any one of the complexans EDTA, MEDTA, CPDTA, CDTA, MCDTA, CHDTA, DPTA, DTPA and NTA allows partial masking.

Zirconium

The ammonia and phosphate precipitations of zirconium are prevented by excesses of EDTA, MEDTA, DTPA, DPTA, CPDTA, CDTA, MCDTA and CHDTA, but masking does not occur with the weaker complexans such as NTA, IDA, MIDA, UDA, CHEL ME, EDDA and AADA.

Thorium

The ammonia precipitation of thorium is masked by the same complexans as for zirconium, but in addition NTA is also effective.

Cerium(IV)

The stronger complexans (column I) are all effective in preventing the ammonia

TABLE IV

REACTIONS OF THE HYDROXIDE-GROUP METALS

Cation	Fe^{+3}			Fe^{+2}		Al^{+3}		Ti^{+4}						Zr^{+4}		Th^{+4}	Ce^{+4}	Be^{+2}	UO_2^{+2}		Cr^{+3}
Anion or reagent	*Thioglycollic acid*	*Ferron*	$Fe(CN)_6^{-4}$	*Dimethylglyoxime*	*o-Phenanthroline*	OH^-	*Alizarin*	OH^-	H_2O_2	H_2O_2	*Cupferron*	*Benzoyl phenyl hydroxylamine*		OH^-	PO_4^{-3}	OH^-	OH^-	OH^-	NH_3	$Fe(CN)_6^{-4}$	OH^-
												–	H_2O_2								
pH[a]	10			H	4.5	H	H		L	N				H		H	H	H	H		H
Medium	NH_3			NH_3	NH_3	NH_3	NH_3							NH_3		NH_3	NH_3	NH_3	NH_3		NH_3
Complexan																					
DHEG																	—	—			
IDA														—	—	—	—	—			
MIDA														—	—	—	—	—			
UDA														—	—	—	—	—			
EDDA														—	—	—	—	—			
AADA														—	—	—		—			
NTA	—	—	—	–	—		—	—	—	—	—	—	±	—	—	+	—	—	—	—	—
CHEL 138																		—	+		
CHELME														—	—	—		—			
EGTA																		—			
HEEDTA	±																	—			+
EDTA	+	+	±	+	—	+	+	—	—	—	—	—	±	+	+	+	+	—	—	+	+
MEDTA	+	+	+	+	—	+	+	—	—	—	—	—	±	+	+	+	+	—	—	—	+
2:3-BDTA	+																				
DPTA	±	+	—	—	—		±	—	—	±	—	—	±	+	+	+	+	—	+	+	+
DTPA	±	+	—		—		+	—	—	—	—	—	±	+	+	+	+	—	—	+	+
CPDTA	±	+	+	+	—	+	+	—	—	±	—	—	±	+	+	+	+	—	—	—	+
CDTA	+	+	+	+	—	+	+	—	—	+	—	—	±	+	+	+	+	—		+	+
MCDTA		+				+				+				+	+	+	+	—			+
CHDTA	+	+	+	+	+	+	+	—	—	+	—	—	±	+	+	+	+	—		+	+

[a] L = low, N = neutral, H = high
Key: See Table II

precipitation of cerium(IV), but precipitation occurs with NTA, IDA, MIDA, EDDA, UDA and DHEG.

Beryllium

None of the complexans masks the precipitation of beryllium hydroxide.

Uranium(VI)

The ammonia precipitation of uranium(VI) is masked only by CHEL 138 and DPTA. Even the strong complexans EDTA, CDTA, MEDTA are ineffective here. The uranyl ferrocyanide reaction is, however, masked by EDTA, DTPA, CDTA and CHDTA in addition to DPTA.

(D) *The alkaline sulphide group*

The sulphide reactions were carried out on $2 \cdot 10^{-2}$ *M* solutions of the metal ions with a one-fold excess of complexan solution and also of sulphide ion.

Cobalt

The precipitation of cobalt as sulphide in an ammoniacal medium is prevented by all the column I complexans, but weaker reagents such as IDA, EDDA, UDA, DHEG, and NTA do not mask the precipitation.

On addition of calcium to the (masked) sulphide solutions partial immediate de-masking (*i.e.* sulphide is deposited) occurs with EDTA, CPDTA and DTPA. MEDTA, CDTA, MCDTA, DPTA and, when heat is applied before addition of sulphide, CHDTA still prevent precipitation though some deposition usually occurs with CDTA on standing for some time.

Nickel

Nickel behaves as cobalt in direct sulphide precipitation in alkaline solution. The de-masking action of added calcium chloride is different, however, for only with the much weaker complexans AADA, UDA, CHEL ME, EGTA, and NTA, does de-masking occur. With EDTA, CPDTA, CDTA, DPTA, DTPA, HEEDTA, 2:3-BDTA, MEDTA and CHDTA (heat as before) masking is still complete. IDA, MIDA, EDDA, DHEG are intermediate in their action.

The precipitation of nickel by dimethylglyoxime in ammoniacal medium is prevented by EDTA, MEDTA, DPTA, DTPA and HEEDTA and also by 2:3-BDTA, CDTA, MCDTA and CHDTA provided that sufficient time is allowed for complete chelation of the nickel by these sterically hindered complexans. In the reverse process it is observed that in all cases the precipitate of nickel dimethylglyoximate dissolves only slowly. The weaker complexans IDA, MIDA, EDDA, CHEL ME, EGTA, UDA, AADA, DHEG, NTA do not prevent qualitative precipitation. It is however known that some of them, though not all, do prevent quantitative precipitation[7].

Zinc

Zinc sulphide is not precipitated by sodium sulphide from a pH 10 (ammonia) buffer in the presence of any of the column I complexans, but weaker reagents such

as NTA still allow deposition. The addition of saturated calcium solution to the masked zinc sulphide causes de-masking, *i.e.* sulphide precipitation, with EDTA, CPDTA, DPTA, DTPA, and MEDTA, but CDTA and CHDTA still mask the reaction.

In an ammonia and ammonium chloride buffer, the precipitation of zinc ferrocyanide is prevented by EDTA, CPDTA, CDTA, MCDTA and CHDTA; IDA, MIDA, AADA, EDDA, UDA, DHEG and CHEL 138 do not prevent precipitation.

Manganese

With manganese, all complexans in column I and NTA prevent precipitation of manganese by sodium sulphide from a pH 10 ammonia buffer. The addition of a strong solution of calcium chloride to each solution causes de-masking (*i.e.* sulphide precipitation) to occur with EDTA and NTA and partial de-masking with CPDTA and MEDTA; CDTA, CHDTA, DPTA, DTPA still hold the manganese in solution.

(*E*) *The carbonate group*

Calcium

All the column I complexans prevent the precipitation of calcium oxalate in ammoniacal solution, but NTA and the weaker complexans do not. In neutral solution only CPDTA, CDTA, CHDTA and possibly DTPA are effective in masking precipitation. Tests with chloranilic acid were not very satisfactory though CDTA and CHDTA effectively mask formation of the microcrystalline precipitate.

Strontium

Strontium is masked against precipitation with oxalate in an ammoniacal medium in the presence of the same complexans as were effective for calcium oxalate; in neutral solution similar results are found except that CPDTA does not prevent precipitation. The reaction of strontium with chloranilic acid is masked by CPDTA, CHDTA and CDTA.

Barium

Barium is masked by the same complexans as strontium in the precipitation of its oxalate from ammoniacal or neutral solutions. None of the complexans appears to mask the precipitation of barium chloranilate or of barium sulphate in neutral or acid solution. The precipitation of barium chromate is masked only by CPDTA in neutral solution though EDTA, MEDTA and CDTA somewhat delay the precipitation. In alkaline solution all the column I complexans except CHDTA prevented precipitation; weak complexans such as NTA do not mask the precipitation. The rhodizonate test for barium in neutral solution is masked by CPDTA, CDTA and CHDTA; partial masking occurs with EDTA and DPTA but DTPA, MEDTA and NTA have no masking action. All these complexans prevent the colour reaction in an ammoniacal medium.

Magnesium

The precipitation of magnesium as phosphate, carbonate or hydroxide is prevented in ammoniacal medium by EDTA and the strong complexans and also by NTA but not by IDA, MIDA, DHEG, AADA, UDA, CHEL ME or EGTA though the precipi-

TABLE V

Cation	Ca^{+2}		Sr^{+2}			Ba^{+2}										Mg^{+2}		
Anion or reagent	*Oxalate*		*Oxalate*		*Chlor-anilic acid*	*Oxalate*		*Chloranilic acid*		SO_4^{-2}		CrO_4^{-2}		*Rhodizonate*		$OH^-PO_4^{-3}$		CO_3^{-2}
pH[a]	*H*	*N*	*H*	*N*		*H*	*N*	*N*	*L*	*N*	*L*	*N*	*H*	*N*	*H*	*H*	*H*	*H*
Medium	NH_3		NH_3			NH_3									NH_3	NH_3	NH_3	NH_3
Complexan																		
DHEG																—	—	—
IDA																—	—	—
MIDA																—	—	—
UDA																—	—	—
EDDA																		
AADA																—	—	—
NTA	—	—	—	—	—	—	—	—	—	—	—	—	—	—	+	+	+	+
CHEL 138																		
CHEL ME																—	±	—
EGTA																—	±	—
HEEDTA																		
EDTA	+	—	+	—	—	+	—	—	—	—	—	±	+	±	+	+	+	+
MEDTA	+	±	+	—	—	+	—	—	—	—	—	±	+	—	+			
2:3-BDTA												—	+					
DPTA	+	—	+	±	—	+	±	—	—	—	—	—	+	±	+			
DTPA	+	±	+	—	—	+	—	—	—	—	—	—	+	—	+			
CPDTA	+	+	+	—	+	+	—	—	—	—	—	+	+	+	+			
CDTA	+	+	+	+	+	+	+	—	—	—	—	±	+	+	+			
MCDTA												—	+					
CHDTA	+	+	+	+	+	+	+	—	—	—	—	—	—	+	+			

[a] L = low, N = neutral, H = high
Key: See Table II

tation is slowed down considerably by UDA and to a lesser extent EGTA and CHEL ME in all cases. CHEL ME and EGTA show a strong tendency to precipitate magnesium from solution as an insoluble salt.

DISCUSSION

The tests described are only qualitative in nature. Thus a reaction which is described above as masked may not be so quantitatively; equally, where there is no apparent diminution in the formation of colour or precipitate the complexan has been described as not interfering though this is not necessarily true on a quantitative basis *cf.* the effect of complexans on nickel dimethylglyoxime[7]. Results differing from those described above may be obtained by variation in the concentrations of reagents. Thus when a strong solution (*i.e.* very large excess) of sodium sulphide is used, a dense precipitate of iron sulphide can be obtained from ferric–EDTA, etc., and similarly zinc sulphide may be precipitated from ammoniacal solutions containing EDTA, CPDTA, CDTA, etc., without the addition of calcium chloride.

SUMMARY

The masking action exerted by 20 complexans on the course of many tests used in the qualitative inorganic analyses of cations is examined and recorded.

RÉSUMÉ

Les auteurs ont examiné l'influence de 20 agents complexants sur différentes réactions de cations en analyse qualitative inorganique.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss von 20 Komplexbildnern auf verschiedene Reaktionen der Kationen bei der qualitativen anorganischen Analyse.

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Book Review

Gas-Chromatographie, par R. KAISER, Akademische Verlagsgesellschaft, Geest & Portig K.G. Leipzig 1960, 223 pages.

Cet ouvrage comprend trois parties principales. Dans la première, l'auteur expose les bases théoriques de la méthode et donne une définition des termes techniques, ainsi que les principales formules qui président aux séparations dans lesquelles interviennent la température, la vitesse du gaz vecteur, la température, etc.

L'appareillage fait l'objet de la deuxième partie; l'étude en est minutieuse; l'auteur donne maints détails sur les colonnes et leur remplissage, sur la purification des gaz vecteurs, sur la mesure de leur vitesse. Des précisions sont données en ce qui concerne les micropipettes et la précision qu'on peut en attendre. Un chapitre est consacré aux détecteurs tels que catharomètres, ionisateurs radioactifs, ionisateurs de flamme et un autre traite des appareils spéciaux et du dosage de traces.

La troisième partie traite des applications tant qualitatives que quantitatives.

Ce qui m'a le plus séduit dans cet ouvrage, c'est la clarté de l'exposé, la façon logique de présenter les divers sujets, l'impression et la disposition du texte qui en font un livre agréable à consulter et qui vous donnent rapidement les renseignements que vous désirez. De plus, il est illustré de quelques photographies et de très nombreux schémas, remarquablement dessinés. Une bibliographie judicieusement établie, des tables de constantes concernant les adsorbants, les phases stationnaires et les coefficients de sélectivité complètent ce livre remarquable.

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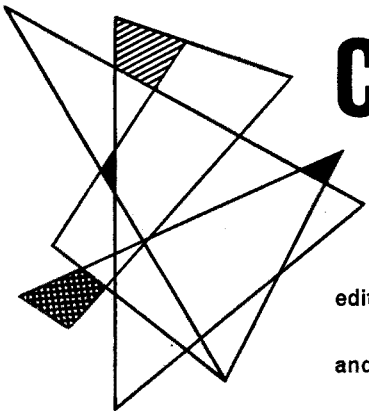

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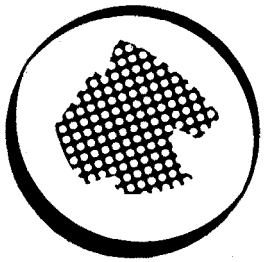

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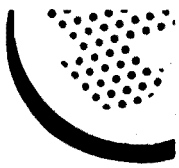

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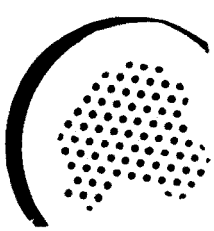

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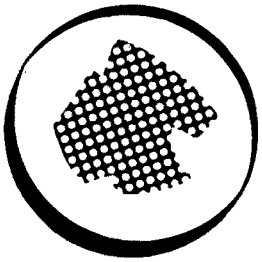

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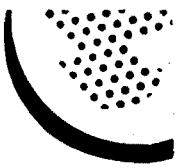

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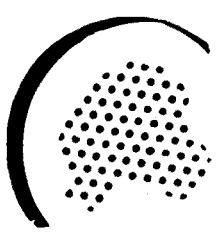

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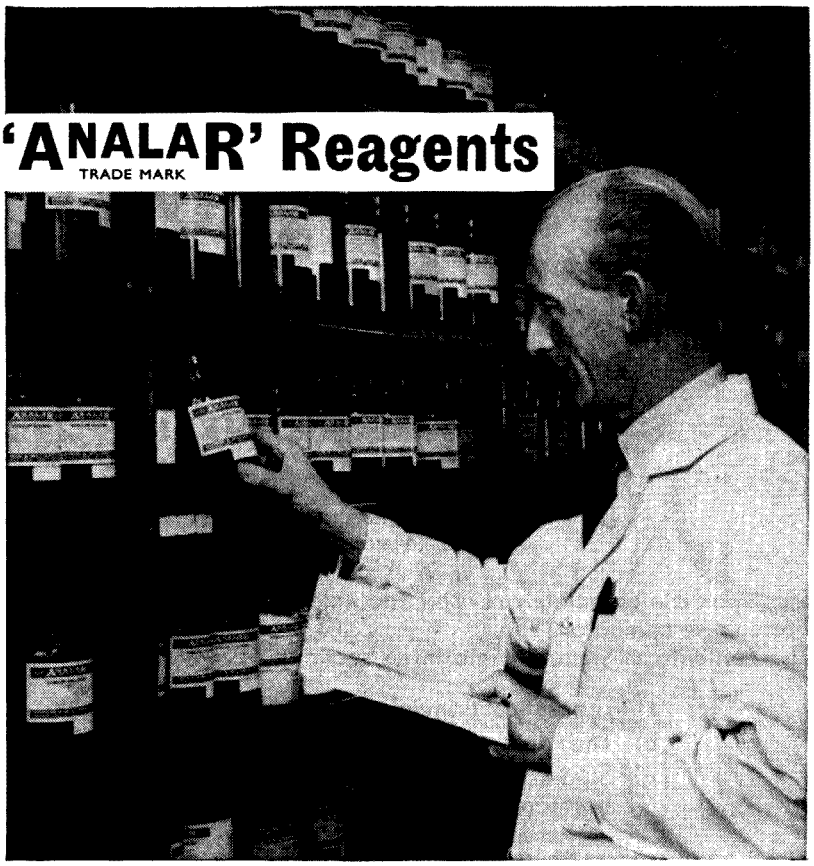

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