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Important Announcement

Professor Philip W. West our American Editor, has been seriously ill. He is now recovering rapidly and should resume his normal editorial activities in a short time. Meanwhile, he has arranged that Dr. J. W. Robinson, a member of the Editorial Advisory Board of this Journal, will carry out his duties. Papers originating in the American Hemisphere can therefore be sent, in the normal way, to **Professor P. W. West, Department of Chemistry, Louisiana State University, Baton Rouge 3, Louisiana.**

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 30, No. 5, May 1964

STUDIES IN THE SOLVENT EXTRACTION OF SOME THALLIUM(I) CHELATES

Studies of the extraction of thallium(I) from aqueous solution into chloroform or MIBK using 6 reagents have been made. Reagent concentration, pH variation, and the addition of adduct-forming agents to the organic phase have all been investigated. Association constants and distribution coefficients for several of the better reagents have been determined. Theoretical interpretations have permitted the identification of participating species and the calculation of equilibrium constants in several cases.

G. K. SCHWEITZER AND G. T. COCHRAN,
Anal. Chim. Acta, 30 (1964) 413–421.

SOLVENT EXTRACTION STUDIES OF ADDITION COMPOUNDS OF METAL HALIDES AND TRIPHENYLPHOSPHINE, -ARSINE AND -STIBINE

PART I. DETECTION OF PALLADIUM

Palladium is very efficiently extracted as $PdI_2 \cdot 2(C_6H_5)_3Sb$ from weakly acidic medium containing excess of iodide with a solution of triphenylstibine in cyclohexane. A test for the detection of palladium is described based on this property. In the presence of sulfite and in the absence of cyanide, which inhibits the reaction, the test is specific. A pink to red color develops in the organic layer enabling the identification of as little as 0.07 μg Pd.

P. SENISE AND F. LEVI,
Anal. Chim. Acta, 30 (1964) 422–426.

ALUMINUM, GALLIUM AND INDIUM CHELATES OF SALICYLIDENE-*o*-AMINOPHENOL

Conditions necessary to determine spectrophotometrically the composition of the chelates of aluminum, gallium, and indium with salicylidene-*o*-aminophenol have been determined. Under these conditions, in each case a chelate containing a 2 : 1 ratio of salicylidene-*o*-aminophenol to metal is formed.

J. H. SAYLOR AND J. W. LEDBETTER,
Anal. Chim. Acta, 30 (1964) 427–433.

THE REACTIONS OF DIPHENYLCARBAZIDE AND DIPHENYLCARBAZONE WITH CATIONS

PART V. EXTRACTION DISSOCIATION CONSTANTS OF THE CARBAZONE COMPLEXES

Extraction experiments in the system water–toluene on the diphenylcarbazone complexes of Mn(II), Fe(II) and (III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(I) and (II), Sn(II) and Pb(II) are described. Only uncharged complexes are formed, the formulae of which are for mercury HgD, Hg(HD)$_2$, Hg$_2$D and Hg$_2$(HD)$_2$ and for the other ions mentioned M(HD)$_n$, depending on the valence n of the cation. The extraction dissociation constants, the molar extinction coefficients and the partition coefficients of the complexes formed by the cations studied were obtained. The complexes prove to be far less stable than the corresponding dithizone compounds so that diphenylcarbazone is less suitable for general analytical use than its sulphur analogue.

S. Balt and E. van Dalen,
Anal. Chim. Acta, 30 (1964) 434–442.

DETERMINATION OF OXYGEN IN URANIUM COMPOUNDS BY REACTION WITH SULFUR MONOCHLORIDE

(in French)

A sulfur monochloride method is proposed for the determination of oxygen in uranium compounds. Sulfur monochloride reacts with oxygenated compounds at temperatures depending upon their nature; the sulfur dioxide produced is titrated by iodometry, after the excess reagent has been eliminated by a selective adsorption–desorption process using activated charcoal. This method has been successfully applied to uranium oxides (UO$_2$, U$_3$O$_8$), to mixtures of uranium dioxide with uranium, uranium nitride, and uranium carbide, and to substituted carbides (UC$_{1-x}$O$_x$). The results are generally satisfactory for oxygen contents higher than 500 p.p.m. However, in the presence of free or combined carbon, this limit is considerably higher. A loss of oxygen as carbon monoxide is also possible, and a simultaneous determination of carbon monoxide must be carried out. The relative error is of the order of a few per cent.

G. Baudin, J. Besson, P. L. Blum and T. V. Danh,
Anal. Chim. Acta, 30 (1964) 443–449.

THE CONDITIONS FOR QUANTITATIVE PRECIPITATION OF PHOSPHATE AS AMMONIUM 12-MOLYBDOPHOSPHATE

The radionuclide phosphorus-32 has been used to measure the effects of (*1*) temperature, (*2*) time of standing, (*3*) stirring, (*4*) the molybdate–phosphate ratio, (*5*) hydrochloric, sulphuric, nitric and perchloric acids, and (*6*) ammonium nitrate on the efficiency of precipitation of ammonium 12-molybdophosphate.

The precipitate is formed quantitatively after 30 min at any temperature between 50° and 80° followed by 30 min at room temperature, provided that the liquid is stirred at 15-min intervals. Twice the stoichiometric amount of nitromolybdate reagent is sufficient for quantitative precipitation. Nitric acid is essential; perchloric acid does not interfere, but hydrochloric and sulphuric acids do. Ammonium nitrate does not affect the efficiency of the precipitation.

D. W. Archer, R. B. Heslop and R. Kirby,
Anal. Chim. Acta, 30 (1964) 450–459.

THERMOGRAVIMETRIC INVESTIGATION OF THE ALKALI METAL DILITURATES

Thermolysis curves for lithium, sodium and cesium diliturates have been obtained. Lithium and sodium dilituratés form monohydrates from aqueous solutions while potassium, rubidium, and cesium dilituratés are anhydrous.

The cesium and rubidium dilituratés form rapidly, are quite dense, and easily handled. Both dilituratés are thermally stable to about 300°. Methods for the thermogravimetric determination of rubidium and cesium have been developed and found to be quite accurate.

M. W. Goheen and R. J. Robinson,

Anal. Chim. Acta, 30 (1964) 460–465.

FLUOROSULPHURIC ACID AS A TITRANT IN ALCOHOLIC SOLVENTS

Fluorosulphuric acid gives highly conducting solutions in alcohols and alcoholic mixtures. Solutions in methanol or in ethylene glycol–methanol give the best results for the direct titration of organic bases, although other alcohols are also satisfactory. Potentiometric and visual methods of end-point detection are suitable.

R. C. Paul and S. S. Pahil,

Anal. Chim. Acta, 30 (1964) 466–472.

THE APPLICATION OF ISOTOPIC DILUTION ANALYSIS TO THE FLUORIMETRIC DETERMINATION OF SELENIUM IN PLANT MATERIAL

A method has been developed for the fluorimetric determination of selenium in plant material using the reagent 2,3-diaminonaphthalene. Oxygen-flask combustion is used to oxidize plant material. Isotopic dilution techniques are incorporated to account for loss in different stages of the procedure. Measurements are also included on the suitability of several other amines as reagents for selenium.

P. Cukor, J. Walzcyk and P. F. Lott,

Anal. Chim. Acta, 30 (1964) 473–482.

THE DETERMINATION OF MANGANESE IN IRON AND STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

A procedure is described for the determination of 0.001–2% of manganese in low and high alloy irons and steels by atomic absorption spectrophotometry. The sample is dissolved in phosphoric–sulphuric acid and atomised in an atomic absorption spectrophotometer. The method is rapid, free from interferences, preliminary separations are not required and results obtained on standard samples agree closely with stated certificate values.

C. B. Belcher and K. Kinson,

Anal. Chim. Acta, 30 (1964) 483–487.

AUTOMATIC ULTRAMICRO DETERMINATION OF IODINE IN NATURAL WATERS

An automatic spectrophotometric reaction rate method is described for the ultramicro determination of iodine in natural waters. The method is based on the catalytic effect of iodine on the reduction of cerium(IV) by arsenic(III). The time required for a small fixed (about 0.06 unit) change in absorbance is measured automatically and related to the iodine concentration. Speed and the small size of the sample needed are the main advantages over other methods. Iodine in water in the range 1 to 15 μg/l in a total volume of 4 ml is determined with errors smaller than ± 0.3 μg/l.

T. P. Hadjiioannou,

Anal. Chim. Acta, 30 (1964) 488–494.

3′,3″-BIS{[N,N-BIS(CARBOXYMETHYL)AMINO]METHYL}-THYMOLSULFONEPHTHALEIN (PENTASODIUM SALT) AS A CHROMOGENIC REAGENT

(Short Communication)

S. C. Srivastava and A. K. Mukherji,

Anal. Chim. Acta, 30 (1964) 495–497.

STUDIES IN THE SOLVENT EXTRACTION OF SOME THALLIUM(I) CHELATES

GEORGE K. SCHWEITZER AND GEORGE T. COCHRAN

Department of Chemistry, University of Tennessee,
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(Received October 4th, 1963)

Thallium(I) extractions

Some of the reagents which have been reported as extractants for the thallium(I) ion are thenoyltrifluoroacetone, diphenylthiocarbazone, sodium diethyldithiocarbamate, mercaptobenzothiazole, and thiosalicylideneethylenediimine[1]. In a recent investigation SCHWEITZER AND NORTON[2] have reported on the use of 14 different chelating reagents as possible extractants for thallium(I). Their results seem to indicate that bidentate 4- and 5-membered chelates bonding through nitrogen and sulfur show the best characteristics for solvent extraction.

The purpose of the present study is to further this work by investigating in detail several extracting reagents for thallium(I), by comparing the efficiencies of extraction with a change in the organic solvent, by analyzing theoretically the extraction data in order to identify the predominating species involved and to estimate association and distribution constants, and by determining the effects of various adducts on the different extraction systems.

Theoretical considerations

In the extraction of thallium(I), the neutral extracting species may be considered to move from an aqueous phase containing the non-complexing perchlorate ion into an organic phase containing a chelating reagent HR, and in some cases, an adduct-forming agent B. Following the selection of a system (organic solvent, HR, B), experiments are conducted which enable the measurement of the distribution coefficient D of the thallium as a function of three variables: the pH, the concentration of the HR, $[HR]_o$, and the concentration of B, $[B]_o$. The data are plotted in terms of curves of log D against each of the variables, holding the other two variables constant. These curves show regions of constant slope and regions of changing slope, the constant-slope regions generally representing conditions under which a single species predominates in each phase.

The value of D on a constant-slope portion of a curve may be approximated by a relationship incorporating one organic species and one aqueous species. For the general case, one can write

$$D = [MR(HR)_a B_b]_o/[MR_r(OH)_h] \qquad (1)$$

where a, b, r, and h have particular integer values, the subscript "o" indicates the organic phase, and the unsubscripted brackets refer to the aqueous phase. By the substitution of appropriate association constants and partition coefficients, eqn. (1) becomes

$$D = K_{1ab}P_{1ab}[HR]_o{}^{1-r+a}[B]_o{}^{b}/K_r{}^{1-r}P_r{}^{1-r+a}P_b{}^{b}C_{rh}K_w{}^{h}[H]^{1-r-h} \qquad (2)$$

where K_{1ab} is the association constant of $MR(HR)_aB_b$, P_{1ab} is the organic/aqueous partition coefficient of $MR(HR)_aB_b$, K_r is the acid association constant of HR, P_r is the organic/aqueous partition coefficient of HR, P_b is the organic/aqueous partition coefficient of B, C_{rh} is the association constant of $MR_r(OH)_h$, K_w is the ion product of water, and [H] is the hydrogen ion activity in the aqueous phase. According to this relation, the slope of a plot of log D against pH at constant $[HR]_o$ and $[B]_o$ will be 1—r—h; the slope of a plot of log D against log $[HR]_o$ at constant pH and $[B]_o$ will be 1—r+a; and the slope of a plot of log D against log $[B]_o$ at constant pH and $[HR]_o$ will be b. Such relations allow reasonable decisions as to the possible species predominating in the two phases on the constant-slope portions of the curves.

Regions in which the slopes of log D plots are changing usually indicate the presence of several species in one phase. The value of D can often be represented by a series of expressions of the form of (2) or reciprocals of (2). Proper slope analysis plus curve fitting then permits in many cases the evaluation of constants and the identification of species.

EXPERIMENTAL PROCEDURES

Thallium-204 in nitric acid, as obtained from the Oak Ridge National Laboratory, was converted to the perchlorate by successive evaporations with perchloric acid. From the product a stock solution was prepared. All chemicals were either reagent grade or were purified by recrystallization procedures. Triisooctylphosphorothionate was purified by passage through a column of Grade F-20 Alcoa alumina. Water was purified by double distillation.

Using 30-ml glass bottles, 10-ml portions of the aqueous phase were stirred with 10-ml portions of the organic phase at 30.0 ± 0.3°. Equilibrium times varied somewhat with the particular system, but all samples were brought to equilibrium. In all cases, the original thallium concentration in the aqueous phase was 10^{-6} M and this phase was also 10^{-1} M in potassium perchlorate. All pH measurements were made on a Beckman Model 76 Expanded Scale pH Meter equipped with a Beckman Combination Electrode. The instrument was calibrated frequently with Coleman buffers at pH values of 2.00, 4.00, 7.00, 9.00, and 11.00, and with 10^{-1} M perchloric acid and sodium hydroxide solutions.

After a given system had reached equilibrium, a 100-μl pipet was employed to sample each phase. The samples were placed onto planchets, dried, and counted with a Tracerlab Beta Scintillation Counter.

In several cases P_r and K_r determinations were made since no data were available in the literature. Ten ml of the organic solvent containing a known concentration of reagent was placed in each of 13 bottles. To each was added 10 ml of 10^{-1} M potassium perchlorate solution, and one sample was adjusted to each pH value from 1.0 to 13.0. After stirring to equilibrium at 30.0 ± 0.3°, a 5-ml sample was removed from the organic phase of each, and by means of a gravimetric determination, the organic/

aqueous distribution ratio of the total reagent d in each of the samples was calculated. In some cases, larger volumes of water had to be equilibrated with the organic phase to make accurate determinations of d. In such cases, gravimetric determinations were carried out on both phases. From a plot of d against pH and the equation $d = K_r\,[H](P_r - d)$, both P_r and K_r were ascertained. A detailed account of the procedure and its use is given by SCHWEITZER AND MOTTERN[3].

RESULTS

Data in Tables

In Table I are presented the results of detailed extraction studies on 28 different

TABLE I

EXTRACTION RESULTS

System[a]	*Data*	*Slopes*
1. $10^{-2.0}$ *M* 2-Mercaptobenzothiazole in $CHCl_3$	pH (log *D*), 6.0 (− 2.43), 7.0 (− 1.31), 7.7 (− 0.64), 8.1 (− 0.14), 8.4 (0.04), 8.7 (0.11), 8.9 (0.20), 9.0 (0.18), 9.3 (0.20), 9.7 (0.20), 10.2 (0.18), 10.4 (0.22), 10.7 (0.20), 11.1 (0.20), 11.3 (0.18), 11.5 (0.10), 11.8 (0.00)	1,0
2. 2-Mercaptobenzothiazole in $CHCl_3$, pH 7.8	log $(HR)_o$ (log *D*), − 3.0 (− 2.52), − 2.5 (− 1.55), − 2.5 (− 1.37), − 2.0 (− 0.52), − 1.5 (0.22)	2
3. 2-Mercaptobenzothiazole in $CHCl_3$, pH 9.0	log $(HR)_o$ (log *D*), − 2.5 (− 0.57), − 2.5 (− 0.52), − 2.0 (0.22), − 1.5 (0.79)	1
4. $10^{-1.7}$ *M* 1,5-Diphenyl-3-thiocarbohydrazide in $CHCl_3$	pH (log *D*), 4.5 (− 1.36), 5.1 (− 0.82), 5.5 (− 0.44), 5.9 (− 0.22), 6.1 (0.00), 6.1 (0.18), 6.7 (0.65), 7.4 (1.36), 7.6 (1.55), 8.0 (1.96), 8.3 (2.36), 9.1 (2.46), 9.5 (2.14), 9.7 (2.15)	1
5. $10^{-1.0}$ *M* 1-Phenyl-2-thiourea in $CHCl_3$	pH (log *D*), 9.9 (− 1.96), 10.4 (− 1.68), 11.0 (− 0.89), 11.9 (− 0.08), 11.9 (0.04)	1
6. $10^{-0.6}$ *M* Thiocarbanilide in $CHCl_3$	pH (log *D*), 8.7 (− 1.18), 8.8 (− 0.95), 9.5 (− 0.18), 9.6 (− 0.07), 9.9 (0.28), 10.0 (0.29), 10.6 (0.97), 11.0 (1.0), 11.2 (1.0)	1,0
7. $10^{-1.0}$ *M* Thiocarbanilide in $CHCl_3$	pH (log *D*), 8.9 (− 1.84), 9.5 (− 0.89), 10.0 (− 0.70), 10.3 (− 0.45), 10.6 (− 0.25), 10.9 (− 0.02), 10.9 (0.22), 11.0 (0.49), 11.2 (0.65), 11.6 (0.84), 12.0 (0.84), 12.1 (0.80)	1,0
8. $10^{-1.5}$ *M* Thiocarbanilide in $CHCl_3$	pH (log *D*), 9.9 (− 1.70), 10.0 (− 1.66), 10.5 (− 1.14), 11.0 (− 0.68), 11.2 (− 0.40), 11.6 (− 0.15), 11.9 (0.30), 12.3 (0.58), 12.5 (0.73), 12.8 (0.56)	1,0
9. Thiocarbanilide in $CHCl_3$, pH 10.0	log $(HR)_o$ (log *D*), − 2 (− 2.3), − 1.5 (− 1.53), − 1.5 (− 1.66), − 1 (− 0.62), − 1 (− 0.72), − 0.8 (− 0.25), − 0.8 (− 0.36), − 0.6 (0.22), − 0.6 (0.23)	2
10. $10^{-2.0}$ *M* Potassium xanthate in water in contact with $CHCl_3$	pH (log *D*), 3.1 (− 2.8), 4.6 (− 1.64), 5.2 (− 0.52), 6.3 (0.61), 6.9 (0.78), 7.4 (0.84), 7.7 (0.86), 8.5 (0.87), 10.0 (0.86)	1,0

System^a	*Data*	*Slopes*
11. Potassium xanthate in water in contact with CHCl$_3$, pH 5.5	log (HR)$_o$ (log D), −3.0 (−1.14), −2.5 (−0.70), −2.0 (−0.18), −1.5 (0.48)	1
12. Potassium xanthate in water in contact with CHCl$_3$, pH 8.0	log (HR)$_o$ (log D), −3.0 (0.87), −2.5 (0.84), −2.0 (0.86), −1.5 (0.86)	0
13. $10^{-1.0}$ M 2-Mercaptobenzothiazole in MIBK^b	pH (log D), 6.2 (−1.70), 7.1 (−0.62), 7.6 (0.04), 8.6 (0.81), 8.7 (0.66), 9.1 (1.21), 9.3 (1.23), 9.7 (1.34), 9.8 (1.40), 9.9 (1.40), 10.2 (1.38), 10.6 (1.40)	1,0
14. 2-Mercaptobenzothiazole in MIBK, pH 7.8	log (HR)$_o$ (log D), −2.5 (−1.85), 2.5 (−1.66), −2.0 (−1.28), −2.0 (−1.30), −1.5 (−0.60), −1.0 (−0.10)	1
15. 2-Mercaptobenzothiazole in MIBK, pH 10.2	log (HR)$_o$ (log D), −2.5 (−0.23), −2.0 (0.43), −2.0 (0.45), −1.5 (0.80), −1.5 (1.00), −1.0 (1.40)	1
16. $10^{-1.5}$ M 1,5-Diphenyl-3-thiocarbohydrazide in MIBK	pH (log D), 4.3 (−1.59), 5.1 (−0.68), 5.9 (−0.06), 7.0 (0.65), 7.0 (1.18), 7.5 (1.20), 7.7 (1.32), 8.2 (2.11), 8.5 (1.97)	1
17. $10^{-1.0}$ M 1-Phenyl-2-thiourea in MIBK	pH (log D), 10.5 (−1.05), 11.0 (−0.68), 11.6 (0.10), 12.2 (0.34)	1
18. $10^{-1.0}$ M Thiocarbanilide in MIBK	pH (log D), 10.0 (−1.48), 10.6 (0.72), 10.6 (−0.69), 10.7 (−0.56), 11.5 (0.24), 11.8 (0.71), 12.1 (0.85)	1
19. Thiocarbanilide in MIBK, pH 11.8	log (HR)$_o$ (log D), −2.5 (−1.54), −2.5 (−1.48), −2.25 (−1.35), −2.25 (−1.46), −2.0 (−1.00), −1.75 (−0.72), −1.75 (−0.68), −1.5 (−0.41), −1.5 (−0.37), −1.25 (0.20), −1.25 (0.18), −1.0 (0.57), −1.0 (0.48)	1,2
20. $10^{-2.0}$ M Thionalide in MIBK	pH (log D), 5.8 (−0.96), 6.9 (−0.15), 7.0 (0.11), 7.4 (0.41), 8.5 (1.47), 9.1 (1.99), 10.1 (2.49), 10.6 (2.35), 11.1 (2.11), 11.5 (1.79), 12.0 (1.32)	1,0,−1
21. Thionalide in MIBK, pH 6.85	log (HR)$_o$ (log D), −2.5 (−0.28), −2.0 (0.23), −2.0 (0.32), −1.5 (0.60)	1
22. Thionalide in MIBK, pH 7.4	log (HR)$_o$ (log D), −2.5 (−0.04), −2.5 (0.00), −2.0 (0.56), −2.0 (0.43), −1.5 (1.24), −1.0 (1.59), −1.0 (1.66), −1.0 (1.75)	1
23. $10^{-1.0}$ M Thiocarbanilide and $10^{-2.0}$ M TOPO^c in CHCl$_3$	pH (log D), 6.5 (−1.30), 7.2 (−0.68), 7.8 (−0.02), 9.0 (0.86), 9.4 (0.96), 9.9 (1.19), 10.4 (1.31), 11.1 (1.38), 11.5 (1.40), 11.5 (1.52)	1,0
24. Thiocarbanilide in CHCl$_3$ and $10^{-2.0}$ M TOPO, pH 7.0	log (HR)$_o$ (log D), −2.5 (−1.74), −2.5 (−1.85), −2.0 (−1.70), −1.5 (−1.35), −1.5 (−1.28), −1.0 (−0.72), −1.0 (−0.68)	1
25. Thiocarbanilide in CHCl$_3$ and $10^{-2.0}$ M TOPO, pH 11.5	log (HR)$_o$ (log D), −2.0 (0.23), −2.0 (0.30), −1.5 (0.78), −1.5 (0.84), −1.0 (1.36), −1.0 (1.41), −1.0 (1.49)	1
26. TOPO in CHCl$_3$ and $10^{-1.0}$ M thiocarbanilide, pH 6.7	log (B)$_o$ (log D), −2.0 (−1.17), −2.0 (−1.11), −1.5 (−0.57), −1.0 (−0.35), −1.0 (−0.24)	1
27. TOPO in CHCl$_3$ and $10^{-1.0}$ M thiocarbanilide, pH 11.5	log (B)$_o$ (log D), −2.5 (1.30), −2.0 (1.40), −1.5 (1.40)	0

System[a]	*Data*	*Slopes*
28. 10^{-2} *M* 2-Mercaptobenzothiazole and 10^{-2} *M* TOPO in $CHCl_3$	pH (log *D*), 5.2 (− 1.80), 6.2 (− 1.15), 6.2 (− 1.04), 6.2 (− 1.00), 7.1 (− 0.32), 8.1 (0.56), 9.0 (0.72), 9.6 (0.69)	1,0

[a] All aqueous phases were $10^{-6.0}$ *M* in radio-labelled thallium perchlorate and $10^{-1.0}$ *M* in potassium perchlorate.
[b] Methyl isobutylketone (MIBK).
[c] Trioctylphosphine oxide (TOPO).

systems. Table II is made up of log P_r and log K_r values, all of which, with the exception of the 2-mercaptobenzothiazole–chloroform values, were determined in this study. The values for mercaptobenzothiazole in chloroform were obtained from the literature[4]. Table III presents a survey of several adduct studies made in an attempt to ascertain the better adduct-forming reagents.

TABLE II

DISTRIBUTION AND ASSOCIATION CONSTANTS OF REAGENTS

Solvent	*Reagent*	*Log P_r*	*Log K_r*
$CHCl_3$	Thiocarbanilide	2.9	11.4
	2-Mercaptobenzothiazole	2.2	7.8
MIBK	Thiocarbanilide	1.0	12.2
	2-Mercaptobenzothiazole	0.94	8.8
	Thionalide	0.6	9.3

Mercaptobenzothiazole systems

Data on mercaptobenzothiazole as an extractant are presented in systems 1, 2, 3, 13, 14, 15, and 28 in Tables I, II, and III. In chloroform (system 1), the log *D* against pH curve rises with a slope of 1, plateaus to a slope of 0, then falls with a changing slope approaching −1. This indicates aqueous species of Tl^+ changing to TlR then to TlR_2^- as the pH rises. Systems 2 and 3 give evidence that at low pH (when the aqueous species is Tl^+) the organic species is TlR·HR, and at higher pH (when the aqueous species is TlR) it is the same. The entire system should be describable by an equation of the following form:

$$\frac{1}{D} = \frac{[Tl]+[TlR]+[TlR_2]}{[TlR\cdot HR]_o} = \frac{[Tl]}{[TlR\cdot HR]_o} + \frac{[TlR]}{[TlR\cdot HR]_o} + \frac{[TlR_2]}{[TlR\cdot HR]_o} \tag{3}$$

Charges on ionic species have been omitted for simplicity. Substituting appropriate terms in the form of reciprocals of (2), one obtains:

$$\frac{1}{D} = \frac{K_rP_r^2[H]}{K_{110}P_{110}[HR]_o^2} + \frac{P_rC_{10}}{K_{110}P_{110}[HR]_o} + \frac{K_r^{-1}C_{20}[H]^{-1}}{K_{110}P_{110}} \tag{4}$$

With P_r and K_r from Table II, log K_{110} P_{110} is calculated to be 7.8, log C_{10} to be 3.2, and log C_{20} to be 3.7.

TABLE III

ADDUCT SURVEY

System[a]	*pH*	*log D*[b]	*log D'*[c]
$10^{-1.0}$ *M* 2-Mercaptobenzothiazole in MIBK with the respective adducts at $10^{-1.5}$ *M*			
Trioctylphosphine oxide	6.6	−1.25	−0.96
Tributylphosphate	6.6	−1.25	−1.25
Dibutyl butyl phosphonate	6.7	−1.19	−1.17
Tributylphosphorothionate	6.9	−1.00	−1.03
Triisooctylphosphorothionate	6.7	−1.15	−1.10
$10^{-2.0}$ *M* 2-Mercaptobenzothiazole in $CHCl_3$ with the respective adducts at $10^{-1.5}$ *M*			
Trioctylphosphine oxide	7.3	−1.05	−0.29
Tributylphosphate	7.5	−0.82	−0.60
Dibutyl butyl phosphonate	7.2	−1.15	−0.92
Tributylphosphorothionate	7.3	−1.05	−0.60
Triisooctylphosphorothionate	7.5	−0.82	−0.25
$10^{-1.3}$ *M* Thiocarbanilide in MIBK with the respective adducts at $10^{-1.5}$ *M*			
Trioctylphosphine oxide	10.4	−1.48	−0.02
Tributylphosphate	10.4	−1.48	−1.04
Dibutyl butyl phosphonate	10.4	−1.48	−1.05
Tributylphosphorothionate	10.3	−1.59	−0.80
Triisooctylphosphorothionate[d]	9.5	−1.22	−0.45
$10^{-1.3}$ *M* Thiocarbanilide in $CHCl_3$ with the respective adducts at $10^{-1.5}$ *M*			
Trioctylphosphine oxide	9.6	−1.78	0.86
Tributylphosphate	9.6	−1.78	−1.70
Dibutyl butyl phosphonate	9.6	−1.78	−1.59
Tributylphosphorothionate	9.6	−1.78	−1.00
Triisooctylphosphorothionate[d]	9.5	−1.22	−0.66
10^{-2} *M* Thionalide in MIBK with the respective adducts at $10^{-1.5}$ *M*			
Trioctylphosphine oxide	6.7	−0.35	−0.66
Tributylphosphorothionate	6.8	−0.22	−1.18
Triisooctylphosphorothionate	6.9	−0.05	−0.75

[a] All aqueous phases were $10^{-6.0}$ *M* in radio-labelled thallium perchlorate and $10^{-1.0}$ *M* in potassium perchlorate.

[b] Value of log *D* without adduct.

[c] Value of log *D* with adduct.

[d] Organic phase of system contained a thiocarbanilide concentration of $10^{-1.0}$ *M*.

System 13 is similar to system 1 except the curve does not begin its drop after the plateau. System 14 appears to call for an organic species of TlR if an aqueous species of Tl^+ is assumed. System 15 would indicate an organic species of TlR·HR if an aqueous species of TlR is assumed. This explanation is not entirely satisfactory, for the authors can see no reason for different organic species when $[HR]_o$ does not change. An alternative explanation in system 15 is that the aqueous species is TlOH and the organic species TlR. This however seems to call for a value of the association constant of TlOH which is much too large compared with literature values[5].

Of 5 different adduct-forming agents (see Table III), triisooctylphosphine oxide (TOPO) appears to enhance the mercaptobenzothiazole extractions the most, and the effects are largest in chloroform. This leads to the detailed data reported under system 28. These data imply that the aqueous species are Tl^+ and TlR as the pH rises, the organic species not being defined by this system. Attempts to determine the $[HR]_o$ and $[B]_o$ dependence were not too successful, but one molecule of each seems to attach to the TlR when it extracts.

Thiocarbanilide systems

Data on thiocarbanilide as an extractant are presented in systems 6, 7, 8, 9, 18, 19, 23, 24, 25, 26, and 27 in Tables I, II and III. In chloroform (systems 6, 7, 8), the log D against pH curves rise with a slope of 1, then plateau to a slope of 0. This indicates aqueous species of Tl^+ and TlR, and the data in system 9 point to an organic species TlR·HR. The log P_r and log K_r values for thiocarbanilide were determined to be 2.9 and 11.4 (Table II). With these, log K_{110} P_{110} was calculated to be 8.7. In MIBK (systems 18, 19) an aqueous species of Tl^+ is indicated by system 18, and the organic species changes from TlR to TlR·HR as $[HR]_o$ increases according to system 19.

As shown in Table III, TOPO in the chloroform system again gives the greatest enhancement of extraction. In detailed studies of this system (systems 23, 24, 25, 26, 27), the indications are that the aqueous species are Tl^+ at low pH and TlR at high pH, and the dominant organic species are TlRB (systems 24, 26) at low pH and TlR·HR (systems 25, 27) at high pH.

Thionalide systems

Data obtained using thionalide as an extractant appear in systems 20, 21, and 22 in Tables I, II, and III. Thionalide could not be used successfully in a chloroform system since the chelate apparently precipitates at the interface, being insoluble in both phases. From the data in Table I, it appears that the aqueous species are Tl^+, then TlR, then TlR_2^- as the pH increases; the organic species is TlR. The values of log K_r and log P_r were determined to be 9.3 and 0.6 and from these log P_{100} was calculated to be 2.5 and log K_{100} to be 2.5. Table III indicates that the extraction was not enhanced by the addition of an adduct-forming agent.

Other systems

Systems 4 and 16 give data on the use of 1,5-diphenyl-3-thiocarbohydrazide as an extractant for thallium(I). In both chloroform and MIBK the aqueous species appears to be Tl^+ and the organic species $TlR(HR)_a$, the a remaining undetermined.

Systems 5 and 17 are concerned with the reagent 1-phenyl-2-thiourea. The results are essentially the same as those for 1,5-diphenyl-3-thiocarbohydrazide.

Systems 10, 11, and 12 report data on the use of the water-soluble reagent potassium xanthate. Indications are that the aqueous species are Tl^+ and TlR, and the organic species is TlR. The log P_{100} can be read from the curve to be 0.9. The log K_r value is reported[6] to be 1.5, but due to a suspicion that the value is in error, no further interpretation was attempted.

GENERAL REMARKS

The shift from chloroform to MIBK as a solvent generally caused extraction to shift toward slightly higher pH values and to higher P_c values. These two observations may be results of the marked solubility of MIBK in water (34 g/l)[7], and of the tendency of the carbonyl oxygen to act as an electron donor thus giving MIBK an adduct character.

The extracting species in the 2-mercaptobenzothiazole–chloroform and thiocarbanilide–chloroform systems was TlR(HR). In the 2-mercaptobenzothiazole–MIBK system the dominant organic species was TlR, and this same species predominated in the thiocarbanilide–MIBK system up to a $[HR]_o$ concentration of about $10^{-1.7}$ M. One might assume that in the chloroform systems the reagent does not have to compete with the solvent for a coordination position on the TlR, whereas in the MIBK systems such competition is of importance.

The differences in the log K_r values in the two solvents as shown in Table II are probably attributable to the high solubility of MIBK in water. Of the 6 reagents studied, all evidenced extractions to give log D values of at least 0.0. Thionalide and 2-mercaptobenzothiazole in MIBK show the best characteristics for possible analytical use, the former being considerably the better of the two.

The adduct studies tend to confirm the idea of solvent competition for a position or positions on the TlR, since the adducts were more effective in the chloroform systems. The most efficient adduct was TOPO, and this is not too surprising in light of its strongly electron-donating oxygen. The observed decrease of extraction efficiency in the thionalide system upon addition of adduct-forming reagents is somewhat puzzling. Perhaps association between HR and B occurs, thereby reducing the effective concentration of HR.

SUMMARY

Studies of the extraction of thallium(I) from aqueous solution into chloroform or MIBK using 6 reagents have been made. Reagent concentration, pH variation, and the addition of adduct-forming agents to the organic phase have all been investigated. Association constants and distribution coefficients for several of the better reagents have been determined. Theoretical interpretations have permitted the identification of participating species and the calculation of equilibrium constants in several cases.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction du thallium(I), au moyen de chloroforme ou de méthyl-isobutylcétone, utilisant 6 réactifs. Ils ont examiné l'influence de divers facteurs et déterminé les constantes d'association et les coefficients de partage de la plupart des meilleurs réactifs. Des interprétations théoriques ont permis l'identification d'espèces participantes et le calcul des constantes d'équilibre dans plusieurs cas.

ZUSAMMENFASSUNG

Die Extraktion von Thallium(I) aus wässriger Lösung mit Chloroform oder Methylisobutylketon mit 6 Reagenzien wurde untersucht. Der Einfluss der Reagenzkonzentration, des pH-Wertes, der Zusatz von Komplexbildnern zur organischen Phase und einige Assoziationskonstanten und Verteilungskoeffizienten wurden bestimmt. Theoretische Deutungen erlaubten die Identifikation der teilnehmenden Verbindungen und in einigen Fällen die Berechnung der Gleichgewichtskonstanten.

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SOLVENT EXTRACTION STUDIES OF ADDITION COMPOUNDS OF METAL HALIDES AND TRIPHENYLPHOSPHINE, -ARSINE AND -STIBINE

PART I. DETECTION OF PALLADIUM

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It is well known that palladium halides and pseudohalides may form addition compounds of several kinds with organic molecules, including phosphines, arsines and stibines. Thus compounds of the formula $PdX_2 \cdot 2(R)_3M$ ($M = P,As,Sb$) may be formed from solutions of the corresponding complex anions $[PdCl_4]^{2-}$, $[Pd(SCN)_4]^{2-}$, etc.[1-7].

Although many of these compounds are known to be soluble in organic solvents it seems that this property has not been used yet for analytical purposes.

In the course of systematic studies carried out in this laboratory on the extractability of phosphonium salts of metal halide and pseudohalide complexes, the unexpected extraction of palladium into some hydrocarbons was traced to the presence of free phosphine[8].

This observation led to a thorough study which showed that, in the presence of excess of iodide, the extraction of palladium into cyclohexane with the help of triphenylphosphine, -arsine and -stibine was highly selective.

On the basis of these findings both a sensitive test of identification and a spectrophotometric method of determination were developed. In this paper the test for the detection of palladium is described.

EXPERIMENTAL

Extraction study

A series of experiments was first run with slightly acidic aqueous solutions of palladium chloride containing excess of halide or pseudohalide ions, *i.e.*, chloride, bromide, iodide, thiocyanate or azide. These solutions were shaken with a 1% solution of triphenylphosphine in the organic solvent. Extraction was evaluated by the intensity of the yellow color of the extract. Palladium was identified by FEIGL's test with mercury iodide[9] following destruction of the organic phase.

Triphenylarsine and triphenylstibine were substituted for triphenylphosphine in two other series of experiments. The color of the organic layer in these cases varied from yellow to red.

Results obtained with cyclic hydrocarbons are summarized in Table I. *n*-Hexane and isooctane in the same conditions proved to be very poor extractants.

TABLE I

EXTRACTION OF PALLADIUM FROM SOLUTIONS CONTAINING HALIDE OR PSEUDOHALIDE IONS AND TRIPHENYLPHOSPHINE, -ARSINE OR -STIBINE[a]

(10 μg Pd in 0.2 ml of aqueous phase extracted with 0.2 ml of a 1% organic solution of the reagent)

		Benzene	*Toluene*	*Ethylbenzene*	*Cyclohexene*	*Cyclohexane*	*2-Methylcyclohexane*
Cl^-	Ph_3P	+++	+++	++	++	o	o
	Ph_3As	+++	+++	+++	o	o	o
	Ph_3Sb	+++	+++	+++	+++	o	o
Br^-	Ph_3P	+++	+++	+++	+++	+	+
	Ph_3As	+++	+++	+++	+	+	+
	Ph_3Sb	+++	+++	+++	+++	++	++
I^-	Ph_3P	+++	+++	+++	+++	+++	++
	Ph_3As	+++	+++	+++	++	+++	++
	Ph_3Sb	+++	+++	+++	+++	+++	++
SCN^-	Ph_3P	+++	+++	+++	++	o	+
	Ph_3As	+++	+++	++	+	++	o
	Ph_3Sb	+++	+++	+	+++	o	o
N_3^-	Ph_3P	+++	+++	++	++	o	+
	Ph_3As	+++	+++	++	++	+++	++
	Ph_3Sb	+++	+++	+	+	++	++

[a] +++ Very well extracted; ++ well extracted; + extracted; o not extracted.

No significant differences were noticed by employing diphenylisopropylphosphine instead of triphenylphosphine.

Experiments were performed also with triphenylbismuthine and no reaction was observed, as might be expected from references in the literature[10,11].

Selectivity and interference study

The extractability of a number of metal ions either in the presence or in the absence of palladium was investigated in preliminary experiments carried out with excess of iodide and 1% solutions of triphenylphosphine, -arsine and -stibine in cyclohexane.

No extraction was observed in the absence of palladium except in the case of platinum when this metal was present in large amounts. Although the extraction was found to depend on the concentration of the reagent in the organic phase, it was observed that in the presence of palladium only very small amounts of platinum could be tolerated. By using triphenylstibine it was found that in the range of 0.1–2 μg Pd, unambiguous identification was possible only if the ratio Pt/Pd was lower than about 20.

It was found, however, that addition of sulfite to the acidic aqueous solution prevented the extraction of platinum as well as the interference of oxidizing agents which converted iodide to iodine, and reacted with the reagent in the organic layer.

A thorough study of the influence of foreign ions was then carried out by performing the test according to the procedure recommended below and taking in every case 1 μg Pd and 1000 μg of the studied ion. The following ions were found not to interfere: Fe(III), Co(II), Ni(II), Ru(III), Rh(III), Os(III), Ir(III), Pt(IV), Cu(II), Ag(I), Au(III), Zn(II), Cd(II), Hg(II), Al(III), Ga(III), In(III), Tl(I), Ge(IV), Sn(IV), Pb(II), As(III), Sb(III), Bi(III), Ti(IV), Zr(IV), V(III), Nb(V), Ta(V), Cr(III), Cr(VI), Mo(VI), W(VI), Mn(II), Mn(VII), U(VI), F^-, Cl^-, Br^-, I^-, SCN^-, OCN^-, N_3^-, NO_3^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_3^-, $S_2O_3^{2-}$, SO_4^{2-}, PO_4^{3-}, PO_3^{3-}, $H_2PO_2^-$.

It should be mentioned that when the influence of Cu(II), Ag(I), Tl(I), Sb(III) and Pb(II) was tested, visualization of the organic layer, if hindered by the precipitate present, was made possible by transferring the extract to another microtube with the help of a capillary dropper.

Cyanide was found to inhibit the reaction completely and should thus be eliminated previously.

The extracted compound

In order to obtain information on the nature of the extracted compound, the product of the reaction between the iodopalladate complex and the organic reagent was isolated and analysed.

1 g of $PdCl_2$ dissolved in about 20 ml of 1 : 1 hydrochloric acid was added to 100 ml of a saturated solution of potassium iodide (approximately 100 g KI) and extraction was performed with 200 ml of a benzene solution of 2.7 g of triphenylphosphine, 3.1 g of triphenylarsine or 3.6 g of triphenylstibine. To the benzene extract 400–500 ml of ethanol were added in order to facilitate the separation of the solid product which was crystallized twice from benzene–alcohol and vacuum-dried at about 60°. The synthesized compounds were all moderately soluble in acetone, benzene and chloroform and insoluble in methanol and ethanol. All were found to decompose on heating above 200°.

$PdI_2 \cdot 2(C_6H_5)_3P$. Yellow crystals. *Anal.* Calcd. for $C_{36}H_{30}I_2P_2Pd$: P, 7.00%; Pd, 12.05%. Found: P, 6.98%; Pd, 11.88%.

$PdI_2 \cdot 2(C_6H_5)_3As$. Brownish yellow crystals. *Anal.* Calcd. for $C_{36}H_{30}As_2I_2Pd$: I, 26.10%; Pd, 10.94%. Found: I, 26.20%; Pd, 10.98%.

$PdI_2 \cdot 2(C_6H_5)_3Sb$. Purplish red crystals. *Anal.* Calcd. for $C_{36}H_{30}I_2PdSb_2$: I, 23.81%; Pd, 9.99%. Found: I, 24.10%; Pd, 10.01%.

Absorption spectra of cyclohexane solutions of the isolated compounds were found to correspond to those of the extracts obtained by the test procedure.

Recommended procedure

To a drop of the slightly acidic solution in a microtube, add a drop of a 40% solution of potassium iodide, a drop of 10% sulfuric acid and 3 drops of a saturated solution of sodium sulfite. Mix and add 2 drops of a freshly prepared — or kept in the dark — 1% solution of triphenylstibine in cyclohexane. Shake and allow the phases to separate. A pink to red color appears in the organic layer if palladium is present. Limit of identification: 0.07 µg Pd.

Owing to the efficiency of the extraction this limit of identification is only slightly affected by dilution. In fact, 0.1 µg Pd could still be detected in 2 ml of aqueous phase.

DISCUSSION

Inspection of Table I shows that other solvents besides cyclohexane might be used in the test as, for instance, benzene or toluene. Cyclohexane was chosen, however, because of its higher selectivity towards iodide with respect to the other anions tested. It was thought that in this manner possible cross-interferences would be prevented. In fact, it was observed that in the presence of excess of thiocyanate, a few metal ions could be extracted with a benzene solution of triphenylphosphine but not extracted with the corresponding cyclohexane solution.

With regard to the choice of solvent it should be added that oxygen-containing compounds, as expected, do not behave as highly selective extractants for palladium. Thus, especially with some ketones and esters, a number of other metal ions would be extracted under the conditions of the test. Some of these solvents, however, if carefully selected, may eventually be used to perform separations of other elements from the aqueous solution following extraction of palladium. Work along these lines is being planned in this laboratory.

If triphenylstibine is replaced by triphenylarsine or triphenylphosphine in the procedure given for the test, the limits of identification will be 0.1 and 0.5 μg respectively, and the extract will be colored yellow. It is interesting to note, however, that the red color of the extract containing $PdI_2 \cdot 2(C_6H_5)_3Sb$ changes to yellow on addition of a 1% solution of triphenylphosphine in cyclohexane, this transformation being irreversible. On the other hand, the yellow color obtained by adding triphenylarsine to the extract, changes back to red on further addition of triphenylstibine. Analogous experiments performed by interchanging triphenylarsine and triphenylphosphine seem to show the predominance of the phosphorus-containing compound. Therefore, as expected[11], the use of triphenylphosphine leads to the most stable compound although, owing to the particular color developed, higher sensitivity is obtained by carrying out the test with triphenylstibine.

Sulfite being absent, the reaction involved in the test can be considered to proceed according to the general equation:

$$PdI_{4(w)}^{2-} + 2\ (C_6H_5)_3M_{(o)} \rightarrow PdI_2 \cdot 2(C_6H_5)_3M_{(o)} + 2\ I^-_{(w)}$$

The analogous reaction with platinum, which also takes place in the absence of sulfite, involves the reduction of tetravalent to divalent platinum under the influence of the reagent as will be shown in a future article.

Addition of sulfite to the red-brown PdI_4^{2-}-containing solution leads to decolorization, indicating that complexation should probably occur. The reaction with triphenylstibine and iodide leading to the same extractable product is nevertheless possible. The inhibiting effect of sulfite on the extraction of platinum(II) may thus be ascribed to its stronger complexing action toward this metal ion.

Although no definite information is yet available regarding the structure of the extracted compound, it is believed, on the basis of preliminary experiments and according to literature data[2,5,10], that it should be the *trans*-isomer of the square planar di-iodo bis(triphenylstibine) palladium complex.

With respect to the applicability of the test it seems worth mentioning that, in contrast to the mercury iodide test[9], solutions of palladium salts treated with ammonia and then reacidified still react under the conditions of the proposed procedure.

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SUMMARY

Palladium is very efficiently extracted as $PdI_2 \cdot 2(C_6H_5)_3Sb$ from weakly acidic medium containing excess of iodide with a solution of triphenylstibine in cyclohexane. A test for the detection of palladium is described based on this property. In the presence of sulfite and in the absence of cyanide, which inhibits the reaction, the test is specific. A pink to red color develops in the organic layer enabling the identification of as little as 0.07 μg Pd.

RÉSUMÉ

Le palladium peut être extrait sous forme de $PdI_2 \cdot 2(C_6H_5)_3Sb$, rouge, en solution légèrement acide, renfermant un excès d'iodure, au moyen d'une solution de triphénylstibine dans le cyclohexane. En présence de sulfite et en l'absence de cyanure, cette réaction est spécifique et permet d'identifier jusqu'à 0.07 μg de palladium.

ZUSAMMENFASSUNG

Palladium wird sehr wirksam als $PdJ_2 \cdot 2(C_6H_5)_3Sb$ aus schwach saurem Medium, das einen Überschuss von Jodid enthält, mit einer Lösung von Triphenylstibin in Cyclohexan extrahiert. Ein Versuch zum Nachweis des Palladiums, der auf diesen Eigenschaften beruht, wird beschrieben. In Gegenwart von Sulfit und in Abwesenheit von Cyanid, welches die Reaktion verhindert, ist der Nachweis spezifisch. Eine rosa bis rote Farbe entwickelt sich in der organischen Phase und ermöglicht den Nachweis von weniger als 0.07 μg Pd.

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ALUMINUM, GALLIUM AND INDIUM CHELATES OF SALICYLIDENE-*o*-AMINOPHENOL

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The present investigation is a continuation of a general program of research on the chelates of aluminum, gallium and indium[1,2] with *o,o'*-dihydroxyazobenzene and related compounds.

Investigations[3-12] of the chelates of salicylidene-*o*-aminophenol have been mainly concerned with the detection and determination of metal ions by the fluorescence of their chelates. By the method of continuous variations, HOLZBECHER[13] was able to establish a 2 : 1 composition for the aluminum(III)-salicylidene-*o*-aminophenol chelate at pH 5. HOVORKA[14] found 2 : 1 chelates with iron(II) and (III), cobalt(II) and (III), and titanium(III) and (IV). Using potentiometric titrations, HOLZBECHER established dissociation constants for the chelates of cadmium(II) and mercury(II). HOLZBECHER[15,16] also studied the fluorescence of chelates as related to the electronic structure of the metal ions and the dissociation constants of the chelates.

EXPERIMENTAL

Apparatus and chemicals

A Cary Model 14 recording spectrophotometer, which has a fluorescence attachment, was used to record the absorption and fluorescence spectra. All pH measurements were made with a Beckman Zero-Matic pH meter calibrated with aqueous buffers. The values of pH refer to the "measured values".

The salicylidene-*o*-aminophenol, abbreviated SAP in this paper, was prepared by the condensation of salicylaldehyde and *o*-aminophenol in 95% ethanol. The SAP was recrystallized from 95% ethanol and its melting point was found to be 187° on a micro hot stage. This product was further purified by sublimation and its ultraviolet and infrared spectra determined.

The indium solution was prepared by dissolving about 0.6 g of indium metal in concentrated nitric acid and diluting to 1 l. The resulting solution was analyzed for indium[17] and found to be $5.09 \pm 0.03 \cdot 10^{-3}$ *M*. The gallium solution was prepared by dissolving about 0.4 g of the metal in concentrated sulfuric acid and diluting to

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1 l. On analysis[18] for gallium, the solution was found to be $5.95 \pm 0.02 \cdot 10^{-3}$ *M*. The aluminum solution was prepared by dissolving about 0.2 g of the metal in 1 : 1 hydrochloric acid and diluting to 1 l. On analysis[19] for aluminum, the solution was found to be $8.07 \pm 0.03 \cdot 10^{-5}$ *M*.

MOLE RATIO STUDIES

On reacting SAP with acid, base and ultraviolet light, the system exhibited a color change from colorless to yellow[20]. Since the photocoloration occurred only in the presence of ultraviolet light, this was eliminated by working in red light. In the case of the acid and base reactions, the situation was more complicated. Since the formation of the chelates required a certain amount of time, the coloration of SAP, as initiated by acid or base, could not be eliminated. It was therefore only possible to describe conditions under which this effect was at a minimum. Considering all existing data, the foremost solution property which regulated the coloration and chelation was the pH. The best conditions for chelation were found by determining the optimum pH. After this pH was found, the chelation of SAP must occur at a greater rate than the color change. This was the crucial point of all chelate studies.

The wavelength for the spectrophotometric determination was determined for each chelate system. In acidic media, with the addition of metal ions to the SAP solution, there were 3 absorbing species, neutral SAP, acidic SAP, and chelate. The metal chelates did not absorb in the same wavelength region as SAP. The chelate had its maximum difference in absorbance from that of SAP at wavelengths greater than 400 mμ (Fig. 1). At these wavelengths, acidic SAP did not absorb. Therefore, the absorbance determinations in this wavelength region were for only two absorbing species, chelate and neutral SAP. For mole ratio studies, only one wavelength was needed.

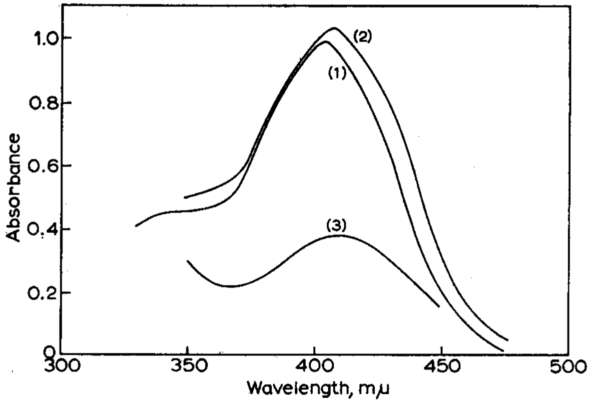

Fig. 1. Absorption spectra of aluminum, gallium and indium chelates of salicylidene-*o*-aminophenol. $1.00 \cdot 10^{-4}$ *M* SAP, $1.00 \cdot 10^{-4}$ *M* metal; curve 1, Al(III), pH 5.00; curve 2, Ga(III), pH 4.50; curve 3, In(III), pH 5.00.

It has been shown previously[20] that the color change does not occur at pH values of less than 3. Therefore, all of the initial chelate solutions had pH values less than 3.

In order to establish the optimum pH for chelation of aluminum(III), gallium(III),

TABLE I

ABSORBANCE OF ALUMINUM–SALICYLIDENE-*o*-AMINOPHENOL AT 405 mμ AS A FUNCTION OF pH AND TIME

(Concentration = $1.00 \cdot 10^{-4}$ *M* SAP and $1.00 \cdot 10^{-4}$ *M* Al(III))

pH	*Absorbance*		
	48 h	*72 h*	*96 h*
2.70	0.000	0.010	0.018
4.00	0.110	0.145	0.173
4.50	0.275	0.347	0.406
5.00	0.920	0.965	0.965
5.50	1.140	1.168	1.192
6.00	1.005	1.070	1.080

TABLE II

ABSORBANCE OF GALLIUM–SALICYLIDENE-*o*-AMINOPHENOL AT 408 mμ AS A FUNCTION OF pH AND TIME

(Concentration = $1.00 \cdot 10^{-4}$ *M* SAP and $1.00 \cdot 10^{-4}$ *M* Ga(III))

pH	*Absorbance*		
	24 h	*72 h*	*96 h*
2.15	0.000	0.013	0.013
3.05	0.050	0.058	0.058
3.60	0.520	0.520	0.520
4.00	0.990	0.990	0.980
4.40	1.040	1.052	1.030
5.00	0.985	1.050	1.023

TABLE III

ABSORBANCE OF INDIUM–SALICYLIDENE-*o*-AMINOPHENOL AT 408 mμ AS A FUNCTION OF pH AND TIME

(Concentration = $1.00 \cdot 10^{-4}$ *M* SAP and $1.00 \cdot 10^{-4}$ *M* In(III))

pH	*Absorbance*			
	24 h	*48 h*	*72 h*	*96 h*
4.05	0.050		0.127	
4.45	0.069		0.182	
4.78	0.148		0.237	
5.00	0.345	0.375	0.400	0.435
5.20	0.142		0.217	
5.42	0.116		0.182	
5.60	0.103		0.170	
5.82	0.107		0.181	

and indium(III), solutions containing $1.00 \cdot 10^{-4}$ SAP, $1 \cdot 10^{-4}$ *M* metal, 0.1 *M* potassium chloride and 3% ethanol were prepared. The pH of each solution was adjusted for the final pH values by the addition of 2 *M* sodium acetate from a micropipet. The ultraviolet and visible absorption spectra were recorded 48, 72 and 96 h after preparation. The data are presented in Tables I, II and III. From these data

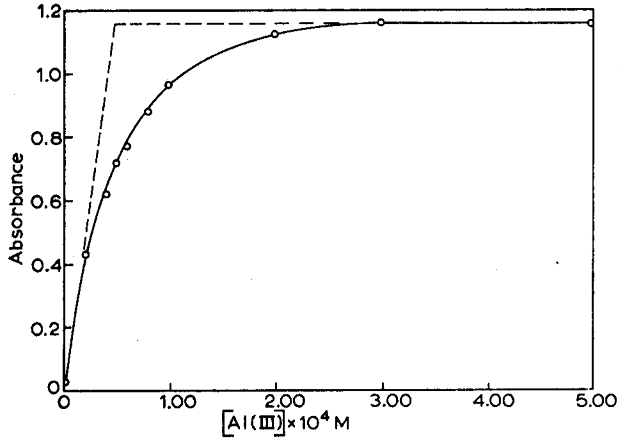

Fig. 2. Spectrophotometric mole ratio plot for aluminum–salicylidene-*o*-aminophenol (96 h after preparation). 1.00 · 10^{-4} *M* SAP; pH 5.00; 405 mμ.

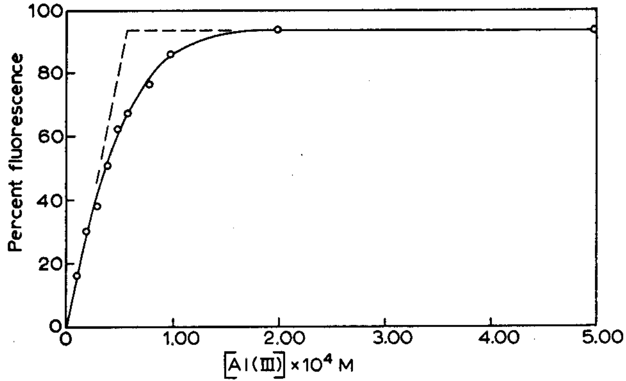

Fig. 3. Fluorimetric mole ratio plot for aluminum–salicylidene-*o*-aminophenol (96 h after preparation). 1.00 · 10^{-4} *M* SAP; pH 5.00; 507 mμ.

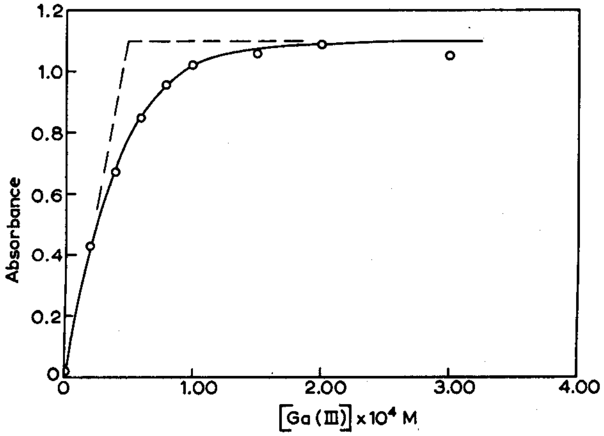

Fig. 4. Spectrophotometric mole ratio plot for gallium–salicylidene-*o*-aminophenol (96 h after preparation). 1.00 · 10^{-4} *M* SAP; pH 4.50; 408 mμ.

the optimum conditions of time and pH for the mole ratio studies were determined. The spectrophotometric data for these studies and the optimum conditions are given in Figs. 2, 4 and 6.

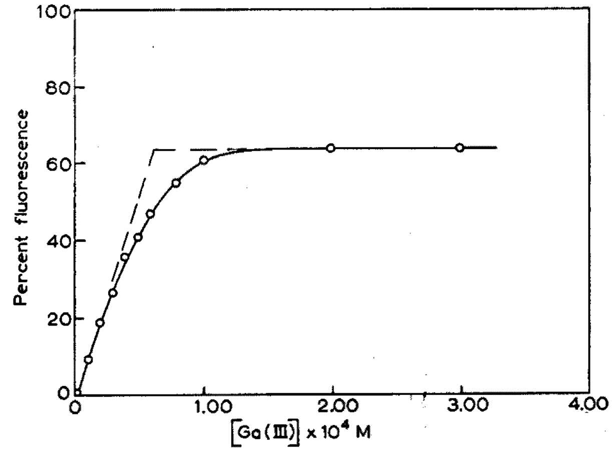

Fig. 5. Fluorimetric mole ratio plot for gallium–salicylidene-*o*-aminophenol (96 h after preparation). 1.00 · 10^{-4} *M* SAP; pH 4.50; 520 mμ.

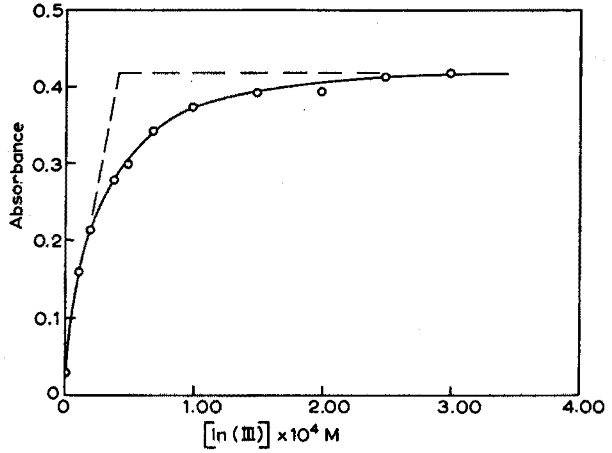

Fig. 6. Spectrophotometric mole ratio plot for indium–salicylidene-*o*-aminophenol (48 h after preparation). 1.00 · 10^{-4} *M* SAP; pH 5.00; 408 mμ.

Fluorimetric spectra for the same solutions were recorded and the data used for the mole ratio plots are given in Figs. 3, 5 and 7. In general, the results from the fluorescence spectra were not as good even though only the chelate fluoresces. This is due to the increase in intensity of the ultraviolet light necessary for fluorimetric determinations. Ultraviolet light inhibits chelation and destroys the chelate after formation causing the mole ratio to be slightly low.

The data indicate in all cases that the composition of each chelate is 2 : 1 (2 SAP : 1 metal) under the conditions of the experiment.

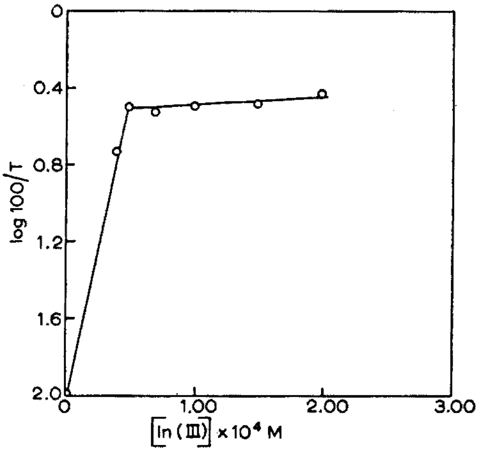

Fig. 7. Fluorimetric mole ratio plot for indium–salicylidene-*o*-aminophenol (48 h after preparation). 1.00 · 10^{-4} *M* SAP; pH 5.00; 515 mμ.

SUMMARY

Conditions necessary to determine spectrophotometrically the composition of the chelates of aluminum, gallium, and indium with salicylidene-*o*-aminophenol have been determined. Under these conditions, in each case a chelate containing a 2 : 1 ratio of salicylidene-*o*-aminophenol to metal is formed.

RÉSUMÉ

Les auteurs ont examiné les conditions nécessaires pour déterminer spectrophotométriquement la composition des chélates d'aluminium, de gallium et d'indium avec le salicylidène-*o*-aminophénol. Dans les conditions décrites, il se forme dans chaque cas, un chélate dont le rapport salicylidène-*o*-aminophénol/métal est de 2 : 1.

ZUSAMMENFASSUNG

Es wurden die Bedingungen untersucht, die zur spektralphotometrischen Bestimmung der Zusammensetzung der Chelate des Aluminiums, Galliums und Indiums mit Salicyliden-*o*-aminophenol nötig sind. Unter den beschriebenen Bedingungen bildet sich in jedem Falle ein Chelat, in dem Salicyliden-*o*-aminophenol und Metall im Verhältnis 2 : 1 vorliegen.

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THE REACTIONS OF DIPHENYLCARBAZIDE AND DIPHENYLCARBAZONE WITH CATIONS

PART V*. EXTRACTION DISSOCIATION CONSTANTS OF THE CARBAZONE COMPLEXES

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In Parts III[1] and IV[2] of this series on the reactions of diphenylcarbazide and diphenylcarbazone, experimental proof has been given that only carbazone complexes are formed. The general formula of the complexes proved to be $M(HD)_n$ according to the valence of the cation. Only mercury(I) and (II) appeared to form more than one complex. This article describes the determination of the extraction dissociation constants of the carbazone complexes in the system water–toluene.

THEORETICAL

The extraction procedure evolved for the dithizone complexes[3] was followed with only some slight modifications.

For the reaction

$$M_w^{n+} + nH_2D_o \leftrightharpoons M(HD)_{n,o} + nH_w^+$$

(w = aqueous phase; o = organic phase)
the extraction dissociation constant K_n is defined as:

$$K_n = \frac{(M^{n+})c_d^n}{c_n(H^+)^n} \tag{1}$$

in which H_2D = diphenylcarbazone; () denotes a concentration in the aqueous phase (only (H^+) means an activity); c a concentration in the organic phase. The index d refers to the carbazone, n to the complex $M(HD)_n$.

If only one complex is formed, c_n and c_d can be calculated from the measured extinctions of the organic phase after the extraction:

$$E = c_n\varepsilon_n + c_d\varepsilon_d \tag{2}$$

(E for 1-cm cuvettes at a fixed wavelength, ε = molar extinction coefficient). (H^+) is found from pH measurements. ε_n can be determined by completely converting a quantity of the carbazone into the complex by shaking with a solution of the cation in excess, as described in Part IV. Under similar conditions the partition coefficient

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* Part IV: *Anal. Chim. Acta*, 29 (1963) 466.

of the complex can be determined. As the original concentrations of both metal ion and carbazone are known, c_n and c_d are easily calculated, and so K_n can be found.

The case of mercury(I) and (II) was more difficult to handle, as both mercury(I) and mercury(II) form more than one complex[1]. Whereas in the dithizone extractions it is possible to select suitable pH ranges in which only one complex has to be taken into account, with diphenylcarbazone the two complexes appeared to be always formed together. Moreover, in the extraction of mercury(I) solutions the disproportionation of Hg_2^{2+} must be taken into consideration[4].

For simplicity, we only assume that besides the 1 : 1 complexes already found, both Hg^{2+} and Hg_2^{2+} form a 1 : 2 compound with the carbazone, an assumption that proves valid in explaining the experimental results. The valences of mercury will be denoted by a second index: I for Hg_2^{2+} and II for Hg^{2+}. As has been proved in Part III for both valences the formula MD is valid for the first complex, so K_1 must be defined as: $K_1 = (M^{2+})c_d/c_1(H^+)^2$.

After the extraction of mercury(II) solutions the extinction of the organic phase at a fixed wavelength is composed as follows:

$$E_{\mathrm{II}} = c_{1,\mathrm{II}}\varepsilon_{1,\mathrm{II}} + c_{2,\mathrm{II}}\varepsilon_{2,\mathrm{II}} + c_d\varepsilon_d \qquad (3)$$

For mercury(I) solutions however:

$$E_{\mathrm{I}} = c_{1,\mathrm{I}}\varepsilon_{1,\mathrm{I}} + c_{2,\mathrm{I}}\varepsilon_{2,\mathrm{I}} + c_{1,\mathrm{II}}\varepsilon_{1,\mathrm{II}} + c_{2,\mathrm{II}}\varepsilon_{2,\mathrm{II}} + c_d\varepsilon_d \qquad (4)$$

As the disproportionation equilibrium constant[4] $k = (Hg_2^{2+})/(Hg^{2+}) = 120$, the quantity of mercury present as free Hg^{2+} ions can be neglected compared with (Hg_2^{2+}).

Defining:

$$\varepsilon_{n,\mathrm{I+II}} = \frac{kK_{n,\mathrm{II}}\varepsilon_{n,\mathrm{I}} + K_{n,\mathrm{I}}\varepsilon_{n,\mathrm{II}}}{kK_{n,\mathrm{II}} + K_{n,\mathrm{I}}}$$

and putting

$$c_{n,\mathrm{I+II}} = c_{n,\mathrm{I}} + c_{n,\mathrm{II}}$$

eqn. (4) becomes:

$$E_{\mathrm{I}} = c_{1,\mathrm{I+II}}\varepsilon_{1,\mathrm{I+II}} + c_{2,\mathrm{I+II}}\varepsilon_{2,\mathrm{I+II}} + c_d\varepsilon_d \qquad (5)$$

Equation (5) is comparable to eqn. (3), with the exception that the constants $K_{n,\mathrm{I}}$ cannot be deduced from eqn. (5) in the same way as the constants $K_{n,\mathrm{II}}$ follow from eqn. (3). Because in eqn. (5) $c_{n,\mathrm{I}}$ has been replaced by $c_{n,\mathrm{I+II}}$, this eqn. will not yield the true constants $K_{n,\mathrm{I}}$, but only "pseudo mercury(I) constants" $K_{n,\mathrm{I+II}}$, differing from $K_{n,\mathrm{I}}$ only in the replacement of $c_{n,\mathrm{I}}$ by $c_{n,\mathrm{I+II}}$.

The relation between the pseudo and the true constants is:

$$(K_{n,\mathrm{I+II}})^{-1} = (K_{n,\mathrm{I}})^{-1} + (kK_{n,\mathrm{II}})^{-1} \qquad (6)$$

Dropping the indices I and II in eqns. (3) and (5), these equations are obtained in the same form which we will write as:

$$E' = c_1\varepsilon_1 + c_2\varepsilon_2 \qquad (7)$$

with

$$E' = E - c_d\varepsilon_d \qquad (8)$$

The ratio $K_{2,\mathrm{II}}/K_{1,\mathrm{II}}$ in the case of mercury(II), or $K_{2,\mathrm{I+II}}/K_{1,\mathrm{I+II}}$ in the case of mercury(I), follows from:

$$\frac{K_2}{K_1} = \frac{c_1}{c_2} \cdot c_d = \frac{(c_1 + c_2)\varepsilon_2 - E'}{E' - (c_1 + c_2)\varepsilon_1} \tag{9}$$

ε_1 is the only constant in eqn. (9) that can be determined separately using the procedure described above for ε_n in eqn. (2). The other constants are evaluated by successive approximation using the following method.

The equilibrium involved takes place in the organic phase and is studied in a series of experiments with a constant value of $c_1 + c_2$ and varying c_d. For every experiment of the series E' and c_d are approximated from eqns. (7) and (8). From the whole series, K_2/K_1 and ε_2 are then calculated also by successive approximation using eqns. (7), (8) and (9).

Experimentally these conditions may be realised by completely extracting a constant amount of Hg^{2+} or $Hg_2{}^{2+}$ with varying excess of the carbazone, or by dissolving varying amounts of the carbazone in a solution of the lowest complex.

The knowledge of the value of the quotient K_2/K_1 allows K_1 and K_2 to be determined separately: K_1 by performing extractions with $c_d \approx c_1$ in which the first complex predominates, and K_2 from extractions with excess of the carbazone where the second complex is the main constituent. In both cases the known value of the quotient K_2/K_1 provides a correction for the other complex present.

A fuller discussion of the above calculations is to be found elsewhere[5].

EXPERIMENTAL

General

Purifications of reagent and solvents were described in the previous papers[1,2,6]. The following p.a. salts already mentioned in Parts III and IV were used in the extractions: the perchlorates of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II); the nitrates of Mn(II), Fe(III), Hg(I), Sn(II) and Pb(II); $FeSO_4$ and CuCl.

The ionic strength of the solutions was kept constant at 0.1 *N* sodium perchlorate because the measurement of extinctions yields concentrations instead of activities. Only the pH can be related to an activity[7]; this quantity was measured with a Philips PR 9400 pH meter using a glass electrode and a saturated calomel reference electrode connected to the solution by an ammonium nitrate bridge to prevent leaking of the potassium chloride into the solution. The pH scale was standardized on Merck Titrisole buffers.

Extinction measurements were performed on a Unicam SP 500 spectrophotometer in 1-cm quartz cuvettes.

The extractions were carried out at room temperature (20–22°).

The volumes of both phases were 25 ml; only for the determination of the partition coefficients, *P*, were larger water volumes used; *P* is defined as:

$$P = \frac{\text{concentration of the complex in the organic phase}}{\text{concentration of the complex in the aqueous phase}}$$

The shaking time was chosen long enough to allow the equilibrium to be fully established. Extinction and pH were measured 1 min after finishing the equilibration.

For the light-sensitive complexes of copper and mercury, darkened glassware was used. Experiments involving the ions Cu^+, Sn^{2+}, Fe^{2+}, Co^{2+} and Mn^{2+} that were readily oxidizable in the experimental conditions, were performed under nitrogen. Nitrogen was also used, if an oxidation of the complexes was probable (for instance, in the determination of the partition coefficients, where large water volumes had to be taken) and at high pH values, where carbon dioxide from the air could interfere.

RESULTS

The complexes obey Beer's law in the concentration region studied (10^{-6}–10^{-4} M). For the cobalt(II) complex this relation could only be verified from 10^{-6} to 10^{-5} M, owing to the minute solubility of this complex in toluene. Complex formation with nitrate and perchlorate was neglected. The values of the concentrations of free M^{n+} in the aqueous phase were calculated with use of the hydrolysis constants taken from the tables of BJERRUM, SCHWARZENBACH AND SILLÉN[8].

$$*K_1 = (M(OH)^{(n-1)+}) \cdot (H^+)/(M^{n+})$$

In Table I the experimental conditions for the determination of the constants K_n are summarized.

The results of the extraction experiments are given in Table II. With the exception of mercury(I) and (II), the formula $M(HD)_n$ was taken for the complex in the calculation of K_n, as described above, in accordance with Part IV of this series. The values of K were found to be constant with varying pH and concentrations of metal ion and reagent; other formulae, *e.g.* $(MD_n)^{n-}$, appeared to cause a drift in the calculated values of K with variation of the pH. Consequently the assumption of uncharged complexes is confirmed.

For some cations, extra information besides the particulars given in the Tables is necessary.

Manganese(II). The extinction was measured at 520 mμ, because the carbazone extinction at the wavelength of maximum extinction of the complex (495 mμ) was too large.

Iron(III). The influence of pH was very important. In the second series of experiments (pH = 1.2–1.6), only Fe^{3+} and $Fe(OH)^{2+}$ were present. In the first series from a pH of about 2.0 on, the hydrolysis equilibrium was rather slowly established; in addition to $Fe(OH)_2^+$, binuclear complexes of formula $Fe_2(OH)_2^{4+}$ have to be taken into account[9].

Iron(II). At the pH values used, any traces of iron(III) that might be formed by air oxidation no longer react with the carbazone. Complex formation between iron(II) and sulphate is negligible[8] under the conditions chosen.

Cobalt(II). The solubility of the complex in toluene is poor (2–$3 \cdot 10^{-5}$ M); moreover the complex is very easily adsorbed on the water-toluene interface. It proved possible to prevent the adsorption by using low concentrations of the complex ($< 10^{-5}$ M) and a large excess of the carbazone. Owing to the large extinction of this excess of carbazone, the spectrum of the complex below 400 mμ could not be measured. The adsorption prevented the determination of P. Because the complex did not colour the aqueous phase in the extractions performed, the value of P must be larger than 10.

Copper(I). In all extractions the aqueous phase contained sodium chloride in a

TABLE I

EXPERIMENTAL CONDITIONS IN THE DETERMINATION OF THE EXTRACTION DISSOCIATION CONSTANTS

Complex	*Shaking time (min)*	*$(M^{n+})\cdot 10^3$ before the extraction*	*$c_a\cdot 10^3$ before the extraction*		*pH range*	*λ ($m\mu$) for the measurement of E*	p*K_1 *used*	*Number of extractions*	*V_w/V_{tol} in the determination of P*
$Mn(HD)_2$	3	2.54 5.34	1.01 1.29	1.60 1.68	6.7–7.7 6.8–7.3	520	9.54	31	20/10
$Fe(HD)_2$	3.5	1.08 2.04	1.00 1.47	1.38 1.98	3.8–4.3 3.9–4.2	510	8.0	21	200/25
$Fe(HD)_3$	1	0.8 1.7	0.5–1.4 1.7–2.1		1.6–2.7 1.2–1.6	505	2.9	30	100/20
$Co(HD)_2$	2	1.28 2.16	0.73 0.79	1.01 1.11	4.3–4.7 4.3–4.7	555	9.0	19	
$Ni(HD)_2$	3	0.95 0.48	1.17 1.44	0.50 1.01	4.3–5.1 4.3–4.8	480	9.4	15	25/25
CuHD	1	0.97 2.70 0.38	0.31 0.41 0.50	0.71	2.4–2.7 1.9–2.5 2.2–2.4	550		16	100/10
$Cu(HD)_2$	1	0.19 0.29	0.10 0.15	0.20 0.31	2.2–3.5 1.9–3.0	550	6.8	31	100/10
$Zn(HD)_2$	2	0.50 1.00	1.05 1.00	1.44 1.51	4.6–5.0 4.5–4.8	550	8.7	15	25/25
$Cd(HD)_2$	2	1.00 2.00	1.40 1.00	0.70 0.51	5.5–6.0 5.5–6.0	485	11.6	17	25/10
$Sn(HD)_2$	1	1.10 0.60	0.71 0.35	0.99 0.50	1.5–2.1 1.6–2.1	545	1.7	24	150/25
$Pb(HD)_2$	2	0.50 1.00	0.86 0.75	1.30 1.00	4.1–4.7 4.1–4.7	540	8.4	31	25/10

TABLE II

PROPERTIES OF THE CARBAZONE COMPLEXES[a]

Complex	K_n *(extraction dissociation constant)*	P *(partition coefficient)*	$\lambda_{max,1}$ *(mμ)*	$\varepsilon_{max,1} \cdot 10^{-3}$	$\lambda_{max,2}$ *(mμ)*	$\varepsilon_{max,2} \cdot 10^{-3}$
$Mn(HD)_2$	$(3.5 \pm 0.8) \cdot 10^{11}$	(0.50 ± 0.15)	285	(25.0 ± 2.0)	495	(24.0 ± 2.0)
$Fe(HD)_2$	$(5.0 \pm 0.7) \cdot 10^{4}$	$(1.2 \pm 0.2) \cdot 10^{3}$	285	(25.1 ± 0.6)	508	(35.7 ± 0.8)
$Fe(HD)_3$	$(8.9 \pm 0.8) \cdot 10^{-2}$	$(2.75 \pm 0.50) \cdot 10^{2}$	284	(29.0 ± 3.0)	507	(50.3 ± 5.0)
$Co(HD)_2$	$(1.0 \pm 0.2) \cdot 10^{7}$	$\geqslant 10$			555	(45.0 ± 4.0)
$Ni(HD)_2$	$(1.2 \pm 0.5) \cdot 10^{6}$	(0.8 ± 0.2)	284	(20.0 ± 3.0)	480	(49.0 ± 6.0)
$Cu(HD)_2$	$(5.4 \pm 0.4) \cdot 10^{-2}$	$(8.8 \pm 2.4) \cdot 10^{2}$	284	(24.0 ± 1.0)	550	(68.0 ± 3.0)
$CuHD$	$(7.4 \pm 1.7) \cdot 10^{-5}$	$(3.3 \pm 0.7) \cdot 10^{2}$	283	(9.8 ± 0.6)	550	(37.5 ± 0.9)
$Zn(HD)_2$	$(5.8 \pm 0.8) \cdot 10^{6}$	(1.3 ± 0.2)	284	(19.2 ± 1.0)	550	(33.0 ± 1.6)
$Cd(HD)_2$	$(1.4 \pm 0.3) \cdot 10^{8}$	(1.10 ± 0.15)	284	(16.3 ± 0.8)	483	(36.7 ± 1.8)
$Hg(HD)_2$	$(5.5 \pm 1.1) \cdot 10^{-6}$	$\pm 1.25 \cdot 10^{3}$			565	(86.0 ± 2.0)
HgD	$(6.1 \pm 1.4) \cdot 10^{-2}$	(6.5 ± 0.2)	284	(12.0 ± 0.3)	550	(32.0 ± 0.8)
$Hg_2(HD)_2$	$(7.7 \pm 1.1) \cdot 10^{-4}$	$\pm 1.25 \cdot 10^{3}$			560	(114.3 ± 2.0)
Hg_2D	(2.3 ± 0.4)	(100 ± 10)	287	(9.0 ± 0.4)	555	(24.8 ± 1.2)
$Sn(HD)_2$	$(8.8 \pm 0.4) \cdot 10^{-3}$	$(2 \pm 1) \cdot 10^{2}$	285	(23.0 ± 3.0)	545	(43.0 ± 5.0)
$Pb(HD)_2$	$(4.0 \pm 0.3) \cdot 10^{5}$	(15 ± 4)	285	(29.2 ± 1.0)	535	(61.3 ± 1.3)

[a] All deviations given are standard deviations.

concentration of 0.5 *M* to prevent oxidation and disproportionation of the copper(I) ion. (Cu^+) was calculated from the constants[8]: $p\beta_2 = -5.0$ and $p\beta_3 = -5.5$, in which for instance $\beta_2 = (CuCl_2^-)/(CuCl)(Cl^-)$. The hydrolysis of copper(I) is negligible at the pH values chosen.

Tin(II). To keep the ionic strength constant, sodium nitrate was used instead of the perchlorate which might be reduced by tin(II). The pH chosen was low enough to prevent the slow hydrolysis of tin(II).

Because of the more complicated character of the systems containing mercury ions, these are described separately. In all experiments the shaking time was 2 min.

In the determination of the partition coefficient, the proportion $V_w : V_{tol}$ for mercury(II) was 500/25, and for mercury(I) it was 200/25.

To determine K_2/K_1, 25 ml of an aqueous phase containing (Hg^{2+}) or $(Hg_2^{2+}) \approx 10^{-5}$ *M* at pH = 3.0–3.5 was extracted with 25 ml of toluene containing the carbazone in varying concentrations (10^{-5} to 10^{-3} *M*). In Fig. 1, E' is plotted against $c_{d,\text{total}}$

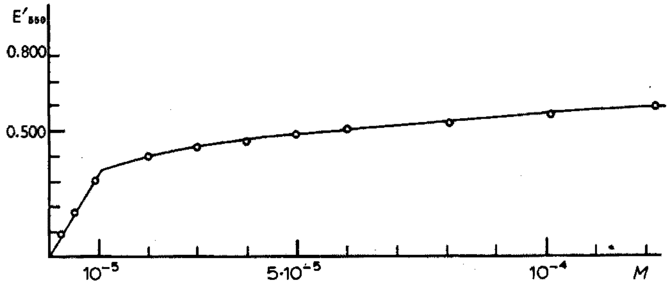

Fig. 1. Extraction of 25 ml of a 10^{-5} *M* mercury(II) perchlorate solution, pH = 3.2, with 25 ml of an increasingly concentrated solution of diphenylcarbazone in toluene.

for a typical experiment for mercury(II), showing that the 1 : 1 complex is formed first. For Hg_2^{2+} similar curves were found. The second part of the curve obeys eqn. (9); by means of this eqn. the following values for the quotient K_2/K_1 were calculated:
for mercury(II): $(1.60 \pm 0.15) \cdot 10^{-4}$ (mean of 22 values),
for mercury(I + II): $(9.0 \pm 1.3) \cdot 10^{-4}$ (mean of 20 values).
Thus for mercury(I), the value is $(2.8 \pm 0.3) \cdot 10^{-4}$ with the help of eqn. (6).

The constancy of these values calculated from eqn. (9) confirms the original assumption that besides the 1 : 1 complexes, only the 1 : 2 complexes $Hg(HD)_2$ and $Hg_2(HD)_2$ are formed, in agreement with the results for the complexes of the other cations studied. The partition coefficients of these 1 : 2 complexes are extremely high: P was found to lie between 1000 and 1500; no precise value could be obtained.

For the determination of K_1, the concentrations of both carbazone and mercury(I) or (II) were chosen near 10^{-5} M. On the other hand, $K_{2,\mathrm{I+II}}$ was calculated from the results of extractions with excess of carbazone (about $5 \cdot 10^{-4}$ M, with (Hg_2^{2+}) about 10^{-5} M). In the experiments mentioned the pH was varied as follows: for $K_{1,\mathrm{I+II}}$, between 2.2 and 2.8, for $K_{2,\mathrm{I+II}}$, between 1.3 and 1.8, for $K_{1,\mathrm{II}}$, between 1.3 and 2.5.

For the pseudo mercury(I) constants the values: $K_{1,\mathrm{I+II}} = 1.7 \pm 0.3$ (mean of 10 values), and $K_{2,\mathrm{I+II}} = (3.2 \pm 0.4) \cdot 10^{-4}$ (mean of 8 values) were obtained. The true constants are mentioned in Table II.

To calculate (Hg^{2+}) a hydrolysis correction proved necessary[10]: $p^*K_1 = 3.70$. For (Hg_2^{2+}), no correction was applied, because[11] $p^*K_1 = 5.0$.

For all K values, a correction for the slow decomposition of the complexes fell within the experimental uncertainty under the conditions given.

For the determination of the extraction dissociation constant K_2 of the very stable mercury(II) complex, a pH below 1.0 was necessary. We did not succeed in determining this constant with an accuracy comparable to the other constants, because of the uncertainty of the pH measurements. Therefore $K_{2,\mathrm{II}}$ was calculated from $K_{1,\mathrm{II}}$ and the quotient $K_{2,\mathrm{II}}/K_{1,\mathrm{II}}$.

Finally it may be remarked that dividing $K_{2,\mathrm{I+II}}$ by $K_{1,\mathrm{I+II}}$ gives $(1.9 \pm 0.3) \cdot 10^{-4}$, which is in agreement with $(1.6 \pm 0.15) \cdot 10^{-4}$, the value found directly with the use of eqn. (9).

DISCUSSION

It is interesting to compare dithizone (diphenylthiocarbazone) and diphenylcarbazone as extraction reagents. In Fig. 2 this is done by plotting the extraction dissociation constants of the carbazone complexes in the system water–toluene, together with the constants[3] of the corresponding dithizone complexes in the system carbon tetrachloride–water. The complexes of diphenylcarbazone prove to be far less stable than the dithizone complexes. However on going from dithizone to diphenylcarbazone not much change in the mutual stability relations of the complexes occurs; only nickel(II) and tin(II) show a difference, the diphenylcarbazone complex of tin(II) being even more stable than its sulphur analogue.

In most cases the low stabilities of the complexes will prevent complete extraction of the cation. This follows from the conditions necessary for carrying out a complete extraction with diphenylcarbazone:

(*1*) The pH must be less than 4.5, because a higher pH greatly enhances the oxidation of the complexes; moreover, higher pH values require a buffer which reduces the effective stability still further by complex formation with the buffer.

(2) c_d must be less than $2 \cdot 10^{-3}$ M to avoid excessive carbazone extinctions.

(3) $(M^{n+})/c_n$ must not exceed 1/50, to keep the deviation from complete extraction below 2% ($V_w = V_o$).

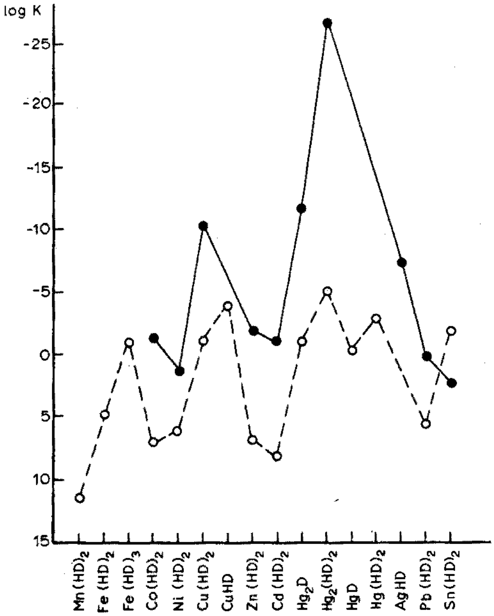

Fig. 2. Comparison of the extraction dissociation constants of diphenylcarbazone and dithizone complexes. H_2D indicates both reagents. ——— Dithizone complexes in the system CCl_4–water; ------ diphenylcarbazone complexes in the system toluene–water.

To meet these demands it is necessary that $K_1 \leqslant 1$, $K_2 \leqslant 10^2$ and $K_3 \leqslant 10^{3.5}$, for uni-, di- and trivalent cations, respectively. Comparison with Table II shows that only iron(III), copper(I) and (II), mercury(I) and (II) and tin(II) can be completely extracted under suitable conditions.

It appears that diphenylcarbazone as an extraction reagent is far less valuable than its sulphur analogue.

It is possible to deduce some indications for the structures of the complexes from the diverse constants and spectra. A detailed account of this work has been given elsewhere[5].

SUMMARY

Extraction experiments in the system water–toluene on the diphenylcarbazone complexes of Mn(II), Fe(II) and (III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(I) and (II), Sn(II) and Pb(II) are described. Only uncharged complexes are formed, the formulae of which are for mercury HgD, $Hg(HD)_2$, Hg_2D and $Hg_2(HD)_2$ and for the other ions mentioned $M(HD)_n$, depending on the valence n of the cation. The extraction dissociation constants, the molar extinction coefficients and the partition coefficients of the complexes formed by the cations studied were obtained. The complexes prove to be far less stable than the corresponding dithizone compounds so that diphenylcarbazone is less suitable for general analytical use than its sulphur analogue.

RÉSUMÉ

Les auteurs ont effectué une série d'extractions de complexes diphénylcarbazone avec Mn(II), Fe(II) et (III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(I) et (II), Sn(II) et Pb(II), en système eau–toluène. Il ne se forme que des complexes non chargés, de formules $M(HD)_n$ (n dépendant de la valence du cation); pour le mercure, il se forme: HgD, $Hg(HD)_2$, Hg_2D et $Hg_2(HD)_2$. Les constantes de dissociation, les coefficients d'extinctions moléculaires et les coefficients de partage des complexes formés par les cations étudiés ont été déterminés. Les complexes correspondants de la dithizone conviennent mieux à un usage analytique général, étant beaucoup plus stables que ceux de la diphénylcarbazone.

ZUSAMMENFASSUNG

Es werden Extraktionsversuche mit den Diphenylcarbazonkomplexen des Mn(II), Fe(II) und (III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(I) und (II), Sn(II) und Pb(II) im System Wasser–Toluol beschrieben. Nur ungeladene Komplexe werden gebildet mit der Formel $M(HD)_n$, bei der n die Valenz des Kations angibt. Für Quecksilber lauten die Formeln: HgD, $Hg(HD)_2$, Hg_2D und $Hg_2(HD)_2$. Die Dissoziationskonstanten, die molaren Extinktionskoeffizienten und die Verteilungskoeffizienten der untersuchten Komplexe wurden bestimmt. Die Komplexe sind weit weniger stabil als die entsprechenden Dithizonverbindungen, so dass Diphenylcarbazon weniger für die Analyse geeignet ist als seine analog Schwefelverbindung.

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DOSAGE DE L'OXYGENE DANS L'URANIUM ET SES COMPOSES PAR LA METHODE AU MONOCHLORURE DE SOUFRE

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Le dosage de l'oxygène dans les métaux fait appel à des méthodes souvent longues et qui nécessitent un appareillage coûteux: extraction sous vide, méthode au trifluorure de brome, spectrographie. En outre, ces méthodes sont quelquefois en défaut. En particulier, si les oxydes présents sont très réfractaires, les résultats obtenus par extraction sous vide sont trop faibles.

La méthode au monochlorure de soufre, proposée par KLEINER, MARKOVA ET OBOLONCHIK[1-3] semble par contre assez simple à mettre en oeuvre et ne nécessite qu'un appareillage courant de laboratoire. Elle a été appliquée avec succès par ces auteurs au dosage de l'oxygène dans les oxydes des métaux suivants: Zr, Ti, Cr, Zn, Mg, Al, Fe, ainsi que dans divers métaux et alliages: Zr, Ti, Cr, Cd, Ni, Cu, (Ni–Mo), (Ni–W).

Nous nous sommes proposés de l'utiliser pour doser l'oxygène dans les composés de l'uranium.

Principe de la méthode

Le monochlorure de soufre réagit avec la plupart des oxydes métalliques à des températures supérieures à 300°, variables suivant la nature de l'oxyde. On obtient les chlorures correspondants, du dioxyde de soufre et du soufre élémentaire[4]:

$$2\ \mathrm{MeO} + 2\ \mathrm{S_2Cl_2} \rightarrow \mathrm{SO_2} + 2\ \mathrm{MeCl_2} + 3\ \mathrm{S}$$

Le dosage du dioxyde de soufre formé permet donc la détermination de l'oxygène contenu dans l'échantillon étudié.

A la température de réaction, les chlorures métalliques formés sont souvent volatils, et se condensent sur la partie froide du tube de réaction. Dans le cas des métaux et des oxydes, on peut vérifier ainsi que la réaction est totale par le fait que la nacelle qui les a contenus se retrouve complètement vide après l'opération.

Le réactif S_2Cl_2 est entraîné dans le four de réaction par un courant d'azote purifié. La présence dans ce réactif de composés oxygénés, tels que SO_2Cl_2 ou $SOCl_2$, susceptibles de fournir également du dioxyde de soufre, fausse évidemment les résultats. Il importe donc de purifier de manière très poussée le monochlorure de soufre ou, mieux encore, de le préparer au moment de l'emploi*.

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* Les détails opératoires seront publiés par ailleurs.

Séparation des gaz SO_2 et S_2Cl_2

Dans tous les cas, la réaction s'effectue avec un excès de réactif, particulièrement dans le cas des oxydes d'uranium où il se forme d'abord l'oxychlorure UO_2Cl_2 qui ne peut être décomposé qu'en présence d'un excès de monochlorure de soufre[5]. Le dosage du dioxyde de soufre étant effectué par iodométrie, il est absolument indispensable d'éliminer cet excès de réactif.

En fait, la séparation des deux gaz est très délicate et représente la difficulté majeure rencontrée au cours de la mise au point de cette méthode.

Les auteurs russes ont utilisé pour absorber l'excès de S_2Cl_2 des sulfures d'antimoine et de mercure qui réagissent, en effet, assez bien à froid avec S_2Cl_2. Cependant des essais à blanc avec ces produits nous ont toujours donné des valeurs considérablement plus élevées que celles annoncées par les mêmes auteurs. Plusieurs tentatives, telles que le chauffage au bain marie de l'absorbeur contenant les sulfures, le chauffage direct des mêmes sulfures dans des nacelles à la sortie du tube de réaction, n'améliorent guère les résultats.

Après étude systématique de divers procédés de séparation chimique ou physicochimique*, nous avons fixé finalement notre choix sur une méthode d'adsorption et de désorption sélective qui, seule, nous a conduit à des résultats satisfaisants. Cette méthode consiste à adsorber sur charbon actif, à une température donnée, les deux gaz et à les désorber sélectivement à des températures différentes. Ainsi à 60° le dioxyde et le monochlorure de soufre sont quantitativement adsorbés; le premier gaz se désorbe à 170°, le second à partir de 230° seulement. Il peut donc être totalement retenu alors que SO_2 est libéré.

En combinant une purification très soignée du réactif S_2Cl_2 avec la méthode de séparation que nous venons de décrire, les valeurs des essais à blanc sont abaissées de façon considérable. Ainsi, pour un débit de gaz de l'ordre de 3 l/h ceux-ci varient de 5 à 6 ml/h d'une solution d'iode 0.1 N quand on utilise l'absorption par les sulfures et du monochlorure de soufre commercial simplement distillé. Ils s'abaissent à 1.5–2 ml/h avec le produit préparé au laboratoire. Si maintenant on utilise la séparation par adsorption–désorption, le blanc n'est plus que de 0.7–1 ml/h d'iode 0.1 N avec le produit rectifié, et 0.06 ml/h avec le produit de laboratoire. Cette dernière valeur, qui correspond à 0.08 mg d'oxygène seulement, peut être considérée comme tout à fait satisfaisante.

Appareillage

L'appareillage (voir Fig. 1) comprend essentiellement un four purificateur du gaz entraîneur, des absorbeurs d'humidité et de dioxyde de carbone, un réservoir contenant le monochlorure de soufre, un tube en U contenant l'adsorbant, un four de réaction, un barboteur, refroidi de préférence, destiné à absorber le dioxyde de soufre que l'on dose par iodométrie. La masse d'oxygène est donnée par la formule:

$$M = 16\,N\,(V_2 - V_1)$$

où N désigne la normalité de la solution d'iode, V_2 le volume de solution d'iode utilisé pour oxyder SO_2 et V_1 le volume d'iode utilisé pour l'essai à blanc.

On remarquera en outre sur la Fig. 1, la présence d'un tube à hémipentaoxyde d'iode

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* Les détails opératoires seront publiés par ailleurs.

placé après l'absorbeur à SO_2. Ce tube est destiné à déceler, et éventuellement à doser les petites quantités de monooxyde de carbone qui sont, comme nous le verrons, susceptibles de se former dans certaines conditions si l'échantillon étudié contient du carbone, et qui, si on les négligeait, introduiraient une erreur systématique par défaut sur la teneur en oxygène.

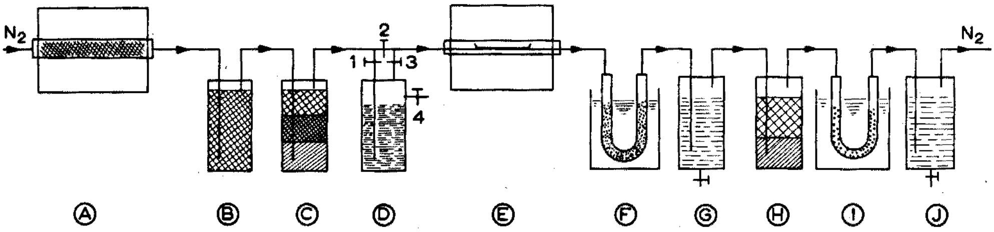

Fig. 1. (A) Four contenant des copeaux d'uranium pour purifier l'azote; (B) absorbeur à gel de silice; (C) absorbeur à gel de silice, à chlorure de calcium et chaux sodée; (D) réservoir de réactif (S_2Cl_2); (E) four de réaction; (F) tube en U avec plaque frittée maintenu dans son bain d'huile; (G) fiole de titrage; (H) absorbeur à chaux sodée et perchlorate de magnésium; (I) tube en U contenant I_2O_5 dans son bain d'huile; (J) absorbeur d'iode.

Les tubes de liaison entre ces divers appareils sont obligatoirement en verre, le caoutchouc et les plastiques étant attaqués par le monochlorure de soufre. Les nacelles sont en graphite.

RÉSULTATS ET DISCUSSION

Oxydes ZrO_2 et HfO_2

Pour éprouver la méthode, nous avons commencé par des essais sur des oxydes facilement attaquables à des températures inférieures à 500°. Parmi ceux-ci, nous avons choisi ZrO_2 et HfO_2 de pureté garantie. Les résultats figurent dans le Tableau I. Ils sont tout à fait satisfaisants.

TABLEAU I

(Composés: ZrO_2 et HfO_2; temps de passage de S_2Cl_2 : 1 h; température de réaction : 500° ± 5°; température de désorption : 170° ± 2°)

Oxydes	*Prise d'essai (mg)*	*Quantité d'iode utilisée, blanc déduit (ml 0.1 N)*	*Masse d'oxygène trouvé (mg)*	*Masse d'oxygène théorique (mg)*	*Erreur relative (%)*
ZrO_2	10	1.64	2.62	2.60	+0.77
	10.3	1.68	2.69	2.68	+0.37
	41	6.50	10.40	10.64	—2.25
	44	7.18	11.49	11.42	+0.61
HfO_2	16	1.56	2.50	2.43	+2.88
	35.2	3.36	5.37	5.35	+0.37
	21	1.92	3.07	3.19	—3.72
	27	2.58	4.13	4.10	+0.73
	49	4.58	7.33	7.45	—1.62
	33	3.14	5.02	5.02	0

Oxydes UO_2 et U_3O_8

La température de réaction reste fixée à 500°. Etant donné la formation très importante de chlorure d'uranium qui se condense sur la partie froide du tube de réaction et qui risque d'absorber une petite quantité de SO_2, nous limitons nos prises d'essais à 50 mg au maximum, valeur qui donne, encore, dans le cas d'oxydes purs une erreur relative assez faible. Les résultats figurent dans le Tableau II.

TABLEAU II

(Composés: UO_2 et U_3O_8; temps de passage de S_2Cl_2 : 1 h; température de réaction : 500° ± 5°; température de désorption : 170° ± 2°)

Oxydes	*Prise d'essai (mg)*	*Quantité d'iode utilisée, blanc déduit (ml 0.1 N)*	*Masse d'oxygène trouvé (mg)*	*Masse d'oxygène théorique (mg)*	*Erreur relative (%)*
	35	2.58	4.13	4.13	0
	35	2.60	4.16	4.13	+0.72
UO_2	44	3.26	5.21	5.19	+0.38
	31.2	2.30	3.68	3.68	0
	41	3.02	4.83	4.84	—0.21
	32	3.12	4.99	4.86	+2.68
	24	2.22	3.55	3.65	—2.58
	29	2.80	4.48	4.41	+1.60
U_3O_8	23	2.16	3.46	3.45	+0.30
	40	3.80	6.09	6.08	+0.17
	47	4.52	7.23	7.14	+1.26
	40	3.78	6.05	6.08	—0.50

Mélanges oxyde–métal et oxyde–nitrure

L'attaque d'un mélange fondu puis pulvérisé UO_2 (70%)–U (30%) se fait bien à 500°.

Celle des mélanges UO_2–UN a déjà une vitesse notable à cette température, mais il y a néanmoins intérêt à opérer à 700°.

Dans les deux cas (Tableau III) les résultats sont satisfaisants.

TABLEAU III

(Composés: mélanges UO_2 + U et UO_2 + UN; temps de passage de S_2Cl_2: 1 h; température de réaction: 700°)

Composition des mélanges (moles %)	*Prise d'essai (mg)*	*Quantité d'iode utilisée, blanc déduit (ml 0.1 N)*	*Masse d'oxygène trouvé (mg)*	*Masse d'oxygène théorique (mg)*	*Erreur relative (%)*
UO_2 (70%) + U (30%) (fondu, pulvérisé)	36	1.95	3.12	3.07	+1.62
UO_2 (50%)	89	3.40	5.44	5.43	+0.20
+ UN (50%)	60	2.20	3.52	3.65	—3.30
(fondu, pulvérisé)	66	2.46	3.94	4.08	—3.50

Mélanges d'oxydes et de produits ou composés carbonés (carbures, oxycarbures, carbone libre)

Les carbures d'uranium sont partiellement attaqués à 500°, mais ne sont totalement décomposés qu'à 700° en chlorures d'uranium, dioxyde de soufre et carbone qui reste dans la nacelle. Cette couche de carbone restant gêne beaucoup l'attaque en profondeur de l'échantillon; c'est pourquoi il faut disposer le produit en couche mince dans la nacelle, et, même pour analyser des échantillons pauvres en oxyde, limiter les prises d'essai à un maximum de 100 mg.

D'autre part, en présence de carbone ou de composés carbonés, on court le risque de perdre une certaine quantité d'oxygène sous la forme de monooxyde de carbone, d'après une réaction analogue à celle d'OERSTED par exemple:

$$\mathrm{MeO} + \mathrm{C} + \mathrm{S_2Cl_2} \rightarrow \mathrm{CO} + \mathrm{MeCl_2} + 2\,\mathrm{S}$$

Cet oxyde de carbone n'étant pas adsorbé par le charbon actif dans les conditions où l'on opère, l'appareillage comprendra dans ce cas un tube à hémipentaoxyde d'iode qui permet de déceler et de doser par la méthode classique l'oxyde de carbone éventuellement formé.

Le Tableau IV rassemble les résultats obtenus.

TABLEAU IV

(Composés: UO_2 + C et UO_2 + UC; temps de passage de S_2Cl_2: 1 h; température de réaction: 700°)

Composition des mélanges (masses %)	*Prise d'essai (mg)*	*Quantité d'iode utilisée, blanc déduit (ml 0.1 N)*	*Masse d'oxygène théorique (mg)*	*Masse d'oxygène sous forme de SO_2, X (mg)*	*Masse d'oxygène sous forme de CO, Y (mg)*	*Total X+Y*	*Erreur relative (%)*
UO_2 (84%) + noir de carbone (16%)	46.2	2.66	4.57	4.26	0.24	4.50	—1.50
UO_2 (88.3%) + noir de carbone (11.7%)	45.2	2.90	4.72	4.64	0.184	4.82	+2.18
UO_2 (86%) + graphite (14%)	40.5	2.60	4.09	4.16	0	4.16	+1.70
UO_2 (81.8%) + graphite (18.2%)	40.9	2.44	3.94	3.90	0	3.90	—1.01
UO_2 (10%) + graphite (90%)	56.7	0.44	0.67	0.70	0	0.70	+4.45
UC (96%) + UO_2 (4%)	102	0.28	0.48	0.45	0	0.48	—6.25
UC (94%) + UO_2 (6%)	105	0.46	0.74	0.73	0	0.74	—1.35
UC (93%) + UO_2 (7%)	103	0.54	0.85	0.86	0	0.85	+1.18
UC (92%) + UO_2 (8%)	75	0.46	0.72	0.74	0	0.72	+2.77
UC (91%) + UO_2 (9%)	72	0.50	0.78	0.80	0	0.78	+2.56
UC (90%) + UO_2 (10%)	56	0.40	0.67	0.65	0	0.67	—3

On remarque immédiatement que seuls les mélanges contenant du carbone libre sous forme de noir conduisent à la formation de monooxyde de carbone, d'ailleurs en petite quantité. Ce gaz n'est pas décelable par contre avec les mélanges UO_2–graphite et UO_2–UC, pour lesquels le dosage de l'oxygène sous forme de SO_2 seulement donne des résultats tout à fait acceptables, quoique moins bons que dans les cas précédents.

Le cas des oxycarbures d'uranium doit être considéré séparément. En effet, pour ces composés, dont la formule reste d'ailleurs discutée, nous n'avons pu disposer que de deux échantillons* dont la teneur en oxygène, déterminée par une autre méthode, n'était donnée qu'à titre indicatif. Les résultats correspondants figurent dans le Tableau V.

TABLEAU V

(Composés: oxycarbures; temps de passage de S_2Cl_2: 1 h; température de réaction: 700°)

Composés	*Prise d'essai (mg)*	*Teneur en oxygène indiquée (masses %)*	*Quantité d'iode utilisée, blanc déduit (ml 0.1 N)*	*Masse d'oxygène nominale (mg)*	*Masse d'oxygène trouvée sous forme de SO_2 (mg)*	*Différence (%)*
Oxycarbure (A)	45	2.57	0.78	1.15_5	1.25	+8.20
$UC_{1-x}O_x$	45.2	2.57	0.72	1.16	1.15	—0.86
	45	2.57	0.76	1.15_5	1.22	+5.60
Oxycarbure (B)	43.6	1.93	0.52	0.84	0.83	—1.19
$UC_{1-x}O_x$	42.7	1.93	0.52	0.82_5	0.83	+0.60

Ces résultats concordent de façon acceptable avec les valeurs fournies. Les différences relatives varient cependant notablement, ce qui tient, en partie au moins, à la faible teneur en oxygène. Elles ne sont pas systématiquement négatives, les écarts les plus forts étant au contraire positifs. Aussi, bien que l'oxyde de carbone n'aie pas été dosé, il est permis de penser qu'il ne s'en forme pas ici en quantité appréciable.

Signalons cependant que des expériences effectuées sur des oxycarbures préparés à notre laboratoire ont donné des résultats qui conduiront peut-être à modifier cette conclusion.

Au total, par conséquent, dans tous les cas où le produit à étudier contient du carbone libre ou combiné, il sera prudent d'utiliser le dispositif de caractérisation et dosage du monooxyde de carbone que nous avons décrit.

CONCLUSION

A condition de prendre quelques précautions, notamment pour la préparation et la purification du monochlorure de soufre, et de prévoir s'il y a lieu la caractérisation et le dosage du monooxyde de carbone, la méthode donne de bons résultats.

La plus petite quantité d'oxygène dosable avec une précision acceptable peut être évaluée à partir de la valeur correspondant à l'essai à blanc, soit 0.08 mg d'oxygène, pour la durée normale d'attaque de 1 h. On estimera par exemple qu'une valeur expérimentale supérieure de 50% à celle correspondant au blanc, donne encore un résultat significatif. Il lui correspondrait, blanc déduit, une masse d'oxygène de 0.04 mg soit, pour une prise d'essai moyenne de 50 mg, une teneur en oxygène de 800 p.p.m.

Nous fixerons donc à 500 p.p.m. la teneur minimale en oxygène, dosable avec une précision suffisante. Cependant, quand l'échantillon contient des carbures, il est prudent d'élever notablement ce minimum, par suite du dépôt de carbone et de le fixer, par exemple, vers 2000 p.p.m. soit 0.2%.

Dans ces limites, l'erreur relative moyenne, variable évidemment avec la teneur en oxygène de l'échantillon, est de l'ordre de quelques pour cent.

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* Fournis par le Centre d'Etudes Nucléaires de Saclay.

RÉSUMÉ

On utilise la méthode au monochlorure de soufre pour doser l'oxygène dans divers composés de l'uranium. Le monochlorure de soufre réagit avec les composés oxygénés (à des températures variables suivant leur nature) en donnant du dioxyde de soufre que l'on dose par iodométrie, après l'avoir séparé du réactif en excès par adsorption–désorption sélective sur charbon actif. La méthode a été appliquée aux produits suivants: oxydes d'uranium (UO_2, U_3O_8), mélanges de dioxyde d'uranium et d'uranium, de dioxyde et de nitrure (UN), de dioxyde et de carbure (UC), carbures substitués ($UC_{1-x}O_x$). Les résultats sont en général satisfaisants pour des teneurs en oxygène supérieures à 500 p.p.m. La présence de carbone libre ou combiné, dans l'échantillon, élève notablement cette limite inférieure. Elle peut également conduire à des pertes en oxygène sous forme de CO, qu'il convient alors de doser en même temps que SO_2. L'erreur relative sur la teneur en oxygène est de l'ordre de quelques pour cent.

SUMMARY

A sulfur monochloride method is proposed for the determination of oxygen in uranium compounds. Sulfur monochloride reacts with oxygenated compounds at temperatures depending upon their nature; the sulfur dioxide produced is titrated by iodometry, after the excess reagent has been eliminated by a selective adsorption–desorption process using activated charcoal. This method has been successfully applied to uranium oxides (UO_2,U_3O_8), to mixtures of uranium dioxide with uranium, uranium nitride, and uranium carbide, and to substituted carbides ($UC_{1-x}O_x$). The results are generally satisfactory for oxygen contents higher than 500 p.p.m. However, in the presence of free or combined carbon, this limit is considerably higher. A loss of oxygen as carbon monoxide is also possible, and a simultaneous determination of carbon monoxide must be carried out. The relative error is of the order of a few per cent.

ZUSAMMENFASSUNG

Es wird ein Verfahren beschrieben, bei dem mit Schwefelmonochlorid in Uranverbindungen den Sauerstoffgehalt bestimmt wird. Das Schwefelmonochlorid reagiert mit Sauerstoffverbindungen unter Bildung von Schwefeldioxid, wobei je nach Verbindung die zu wählende Temperatur eigens festgelegt werden muss. Das überschüssige Schwefelmonochlorid wird dann mit Hilfe eines selektiven Adsorption-Desorption Verfahrens mit Aktiv-Kohle entfernt und das Schwefeldioxid jodometrisch bestimmt. Diese Methode erlaubt die Untersuchung folgender Verbindungen: Uranoxid (UO_2,U_3O_8), Mischungen von Urandioxid mit Uran bzw. mit Uran-Nitriden oder Uran-Carbiden, substituierte Carbide ($UC_{1-x}O_x$). Für Proben mit mehr als 500 p.p.m. Sauerstoff sind die Ergebnisse sehr befriedigend. In Anwesenheit von freiem oder gebundenem Kohlenstoff muss diese untere Grenze bedeutend erhöht werden. Ebenso ist in Gegenwart von Kohlenstoff ein Verlust an Sauerstoff durch Bildung von Kohlenmonoxid möglich; in diesem Fall muss das Kohlenmonoxid gesondert bestimmt werden.

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THE CONDITIONS FOR QUANTITATIVE PRECIPITATION OF PHOSPHATE AS AMMONIUM 12-MOLYBDOPHOSPHATE

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Several workers, notably THISTLETHWAITE[1] and STOCKDALE[2], have investigated ammonium 12-molybdophosphate and its formation, but although the precipitation of this compound remains one of the principal methods for the determination of phosphorus, there is still some disagreement about the best conditions for the formation of the precipitate. The radioisotope phosphorus-32 has now been used to study the effects of several factors on the efficiency of precipitation of phosphate ions as ammonium 12-molybdophosphate.

(*1*) *The range of temperature over which the compound is precipitated quantitatively.* Although it is generally accepted that the precipitation of ammonium 12-molybdophosphate is affected by temperature, there is disagreement about the optimum temperature. The British Standard methods[3,4] recommend 80°, STOCKDALE[2] 60°, THISTLETHWAITE[1] 50°, KITAHARA[5] 45° and CANNON[6] 40°.

(*2*) *The time necessary.* Several authors report the effect of leaving the precipitate to stand in the presence of the supernatant liquid. For complete precipitation, THISTLETHWAITE[1] allowed 1 h at 50° and 1.25 h at room temperature, STOCKDALE[2] 1 h at 60°, CANNON[6] 1 h at 40° and 24 h at room temperature.

(*3*) *The amount of stirring required.* The British Standard methods, THISTLETHWAITE[1] and CANNON[7] do not recommend stirring the solution when forming the precipitate, but STOCKDALE[2] advocated that it should be stirred for 1 min every 15 min.

(*4*) *The stoichiometric amount of molybdate reagent needed.* THISTLETHWAITE[1] considered that at least 3.5 times the stoichiometric amount of molybdate reagent for the reaction

$$PO_4^{3-} + 12\ MoO_4^{2-} + 24\ H^+ \rightarrow PMo_{12}O_{40}^{3-} + 12\ H_2O$$

was necessary for quantitative precipitation of the phosphate.

(*5*) *The effect of various acids.* There is general agreement that the ammonium 12-molybdophosphate precipitate can be formed only in acidic solutions. Sulphuric and hydrochloric acids are unsatisfactory because they react with the precipitate, but both nitric and perchloric acids have been used. STOCKDALE[2] and CANNON[7] both found that a large excess of nitric acid prevented full precipitation. THISTLETHWAITE[1] found that the most consistent results were obtained from a nitric acid/ammonium molybdate mixture made at least 24 h before it was required for use.

(6) *The effect of ammonium nitrate on the precipitation.* Ammonium nitrate was formerly thought to be necessary for the precipitation. FREY[8] found that its use increased the weight of the precipitate; STOCKDALE found it to be unnecessary unless the nitric acid was very concentrated, but CANNON[7] considered that a large excess of ammonium nitrate improved the precision of the method.

EXPERIMENTAL

(1) *General procedure*

(a) *Preparation of potassium dihydrogen phosphate solution*

A solution was prepared containing 1.28 g of dried potassium dihydrogen phosphate per litre.

(b) *Preparation of nitric acid/ammonium molybdate reagent*

Except for the experiments in 2(f) below, the reagent was made by the method advocated by THISTLETHWAITE[1]. Powdered A.R. ammonium molybdate (35 g) was dissolved in a mixture of 50 ml of aqueous ammonia (0.880) and 50 ml of water. Concentrated nitric acid (168 ml, s.g. 1.42) was diluted to 360 ml with water and allowed to cool. The ammoniacal ammonium molybdate solution was poured into the nitric acid in a thin stream, with constant stirring. This solution was allowed to stand for 24 h, diluted to 900 ml with water, filtered, and stored in polythene containers. This solution was used in all experiments except those under 2(f).

(c) *Phosphorus-32*

The radioisotope, phosphorus-32, was obtained as phosphoric acid from The Radiochemical Centre, Amersham. It is essential that the radiophosphorus is in the same oxidation state as the orthophosphate used in the experiments; the following solutions were pipetted into a small beaker in the order shown, and mixed thoroughly: 2.5 ml of concentrated hydrochloric acid, 1 ml of 100-volume hydrogen peroxide, 2.5 ml $M/60$ potassium dihydrogen phosphate, and 40 μC of phosphorus-32.

The beaker was covered with a watch-glass; the mixture was warmed on a hot plate for 15 min and diluted with water to 100 ml.

(d) *Counting equipment*

The β-emission from the phosphorus-32 was counted using a Mullard MX 124 liquid counter and an ECKO N530F Automatic Scaler. Experiments were designed to give at least 10,000 counts so that the standard deviation did not exceed 1%. In most of the experiments with phosphorus-32, the amount of phosphate removed from the solution closely approached 100%. As accurate counts on the filtrate were required, the quantity of active phosphate added was necessarily rather high.

(e) *Temperature control*

The temperature was controlled in an external water bath heated by a 1 kV "Techne Tempunit" thermostatic head. The selected temperature was maintained to within ± 0.05°.

(*f*) *Analytical procedures*

(*1*) *Molybdenum.* Ammonium 12-molybdophosphate was dissolved in the minimum amount of 1.0 *M* sodium acetate (pH 8.7) and diluted with 50 ml of water. The solution was brought to boiling point, and molybdenum was precipitated as oxinate by the dropwise addition, with continuous stirring, of a 2% oxine reagent. This reagent was made by dissolving 5 g of 8-hydroxyquinoline in 22.3 ml of glacial acetic acid diluted with a little water; a solution of 17 g of sodium acetate was added and the solution was diluted to 250 ml. The dropwise addition of the reagent was continued until the liquid became yellow; then about 0.5 ml more of the reagent was added. The liquid was boiled gently for 5 min, and the precipitate was then collected, washed with hot water, and dried at 130°.

(*2*) *Phosphorus.* (*a*) *As lead phosphate.* The filtrate and washings from (*1*) were adjusted to pH 5.8 by the addition of 1.0 *M* caustic soda. The liquid was filtered, made up to 300 ml and heated to boiling. The phosphate was precipitated by adding dropwise, with continuous stirring, a solution containing 3 g of A.R. lead acetate in 1 l of 0.01 *N* acetic acid until precipitation was complete. The liquid was heated to 90–100° for 30 min and set aside for 24 h. The precipitate was filtered, washed with hot water and dried at 130–140°. (*b*) *As magnesium ammonium phosphate hexahydrate.* Ammonium 12-molybdophosphate was dissolved in the minimum amount of dilute aqueous ammonia. This solution was rendered slightly acid to methyl red with dilute hydrochloric acid; magnesia mixture was added dropwise with continuous stirring, followed by excess of ammonia, and the liquid was allowed to stand overnight. The supernatant liquid was filtered without attempting to transfer the precipitate. The residue on the filter was washed with 1 *M* aqueous ammonia and then dissolved in warm 2 *M* hydrochloric acid. This solution was returned to the beaker containing the remainder of the precipitate. The solution was diluted to 100 ml and 2 ml of magnesia mixture were added. The phosphate was re-precipitated by adding, with continuous stirring, 50% aqueous ammonia in excess, and allowed to stand overnight. The precipitate was filtered and washed with 1 *M* ammonia until free from chloride, then with alcohol, and finally with anhydrous ether. The precipitate was placed in a desiccator for at least 30 min and weighed as $MgNH_4PO_4 \cdot 6H_2O$.

(*3*) *Ammonium as ammonia.* Ammonium 12-molybdophosphate was dissolved in aqueous sodium hydroxide. The mixture was distilled and the ammonia, liberated quantitatively, was absorbed in an excess of standard acid. The excess of acid was back-titrated with standard caustic soda with methyl red as indicator.

(*g*) *Wash solutions*

(*a*) *Acid ammonium nitrate.* 20 g of A.R. ammonium nitrate and 12.5 ml of nitric acid (s.g. 1.42) were made up to 2.5 l with distilled water. (*b*) *Nitric acid.* A 1% solution was prepared.

(*h*) *Sintered glass filters*

The filters were of porosity 4.

(*2*) *Factors governing the efficiency of precipitation of ammonium 12-molybdophosphate*

(*a*) *The time and temperature necessary for quantitative precipitation of phosphate*

Ammonium molybdate (4 ml) was added to potassium dihydrogen phosphate (2 ml), containing about 0.5 μC phosphorus-32, in a series of experiments at different temperatures. The solution, which was stirred every 15 min with a glass rod, was maintained at the selected temperature and then for the same period of time at room temperature. The ammonium 12-molybdophosphate was filtered, washed with acid ammonium nitrate solution and given a final wash with nitric acid (1%). A count was taken on the combined filtrate and washings and on the ammoniacal extract of the ammonium 12-molybdophosphate. The percentage of phosphorus precipitated was calculated from the corrected count-rates. The results are shown in Table I.

TABLE I

EFFECT OF TEMPERATURE AND STANDING TIME

Precipitation temperature (T°)	*% Phosphorus precipitated*			
	Time at T°	*15 min*	*30 min*	*60 min*
	Time at room temperature	*15 min*	*30 min*	*60 min*
30		98.22±0.01	99.49±0.02	99.60
40		97.90±0.10	99.50±0.10	99.81
50		98.20±0.10	99.88±0.02	99.93
60		98.60±0.20	99.90	99.96
70		98.97±0.10	99.93	99.96
80		99.30±0.10	99.97	99.98
90		99.70	99.97	99.97

(*b*) *The composition of the precipitate at 80° and at 90°*

Ammonium molybdate (4 ml) was added to potassium dihydrogen phosphate (2 ml) at 80°. The solution, which was stirred every 15 min, was maintained at this temperature for 1 h and at room temperature for 1 h. The ammonium 12-molybdophosphate was filtered, washed with 1% nitric acid and dried at 200° for 24 h. The experiment was repeated at 90°. The weights of precipitate obtained are shown in Table II.

TABLE II

COMPOSITION OF THE PRECIPITATE

Theoretical weight of $(NH_4)_3[P(Mo_3O_{10})_4]$ *(g)*	*Weight of precipitate found (g)*	
	80°	*90°*
0.0353	0.0350–0.0362 Mean 0.0356	0.0855–0.0922 Mean 0.0887

These precipitates were analysed with the results shown in Table III. The precipitate formed at 90° was a paler yellow and was contaminated with a white solid. The precipitates were analysed for nitrate, but it was absent.

(*c*) *The effect of stirring with a glass rod compared with reliance on convection currents for mixing*

Ammonium molybdate (4 ml) was added to potassium dihydrogen phosphate (2 ml), containing about 0.5 μC of phosphorus-32, at 70°. The solution, which was

TABLE III

ANALYSIS OF THE PRECIPITATES FORMED

	% Found		*% Calculated for $(NH_4)_3PMo_{12}O_{40}$*
	80°	*90°*	
Molybdenum	60.9–61.3 (Mean 61.1)	60.6–61.0 (Mean 60.8)	61.3
Phosphorus as $Pb_3(PO_4)_2$	1.66–1.69 (Mean 1.68)	0.67–0.71 (Mean 0.69)	1.65
Phosphorus as $MgNH_4PO_4 \cdot 6H_2O$	1.64–1.68 (Mean 1.66)	0.68–0.71 (Mean 0.70)	1.65
Ammonium	2.24–2.84 (Mean 2.76)	1.67–1.92 (Mean 1.82)	2.88

stirred every 15 min, was maintained at this temperature for 1 h and at room temperature for 1 h. The ammonium 12-molybdophosphate was filtered and washed as in experiment (*a*) above. The experiment was repeated without stirring.

The experiment was repeated at 80° but the time at this temperature was increased to 2 h. The percentage of phosphorus precipitated was calculated from the corrected count-rates on the combined filtrate and washings and on the ammoniacal extract of the ammonium 12-molybdophosphate. The results are shown in Table IV.

TABLE IV

EFFECT OF STIRRING

Precipitation temperature (°)	*Time in thermostat (h)*	*Time at room temperature (h)*	*% Phosphorus precipitated*	
			Stirring by glass rod	*No stirring*
70	1	1	99.97 ± 0	99.30 ± 0.5
80	2	1	99.88 ± 0.10	99.89 ± 0.03

(*d*) *The effect of adding excess of the molybdate reagent*

Different amounts of ammonium molybdate were added to potassium dihydrogen phosphate (2 ml), containing about 0.5 µC of phosphorus-32, at 70° and at 80°. The solution, which was stirred at 15-min intervals, was maintained at the required temperature for 1 h and at room temperature for 1 h. The ammonium 12-molybdophosphate was filtered and washed as in experiment (*a*) above. Counts were taken on the combined filtrate and washings and on the ammoniacal extract of the ammonium 12-molybdophosphate. The percentage of phosphorus precipitated was calculated from the corrected count-rates; results are shown in Table V. The weight of precipitate obtained from potassium dihydrogen phosphate (2 ml) and ammonium molybdate (2 ml) at 70° was found to be 0.0354–0.0360 g. The mean weight was 0.0356 g (weight based on $(NH_4)_3[P(Mo_3O_{10})_4]$ is 0.0353 g).

TABLE V

EFFICIENCY OF PRECIPITATION OF AMMONIUM 12-MOLYBDOPHOSPHATE

Amount of ammonium molybdate added to 2 ml of phosphate solution (ml)	*Stoichiometric ratio of molybdate to phosphate ($12\ MoO_4^{2-} : 1\ PO_4^{3-} = 1$)*	*% Efficiency*
1	0.88	75.04
1.15	1.0	84.63
1.25	1.1	98.63
1.4	1.2	98.77
1.5	1.3	98.80
1.6	1.4	99.38
1.7	1.5	99.47
1.85	1.6	99.58
2.0	1.75	99.91
2.3	2.0	99.90
3.0	2.6	99.95
4.0	3.5	99.95
5.0	4.4	99.98
6.0	5.25	99.98

(*e*) *The effect of some mineral acids on the precipitation of ammonium phosphomolybdate*

Ammonium molybdate (4 ml) was added to potassium dihydrogen phosphate (2 ml) containing about 0.5 µC phosphorus-32, at 70° and also at 80°. Different amounts of nitric acid (s.g. 1.42) were added to the mixture (Table VI). The mixture, which was stirred every 15 min, was maintained at the required temperature for 1 h and at room temperature for 1 h. The ammonium 12-molybdophosphate was filtered and washed as in experiment (*a*). Counts were taken on the combined filtrate and washings and on an ammoniacal solution of the precipitate. The percentage of phosphorus precipitated was calculated from the corrected count-rates. The experiment was repeated using sulphuric (s.g. 1.84), hydrochloric and perchloric acids and the results are listed in Table VII. The weight of ammonium 12-molybdophosphate precipitated

TABLE VI

EFFECT OF NITRIC ACID CONCENTRATION

Amount of nitric acid added (ml)	*Molarity of nitric acid in final solution*	*% Phosphorus precipitated*	
		70°	*80°*
1	3.8	99.95	99.93±0.01
2	5.4	99.91	99.94
3	6.5	99.91	99.90
4	7.5	99.85±0.10	99.82±0.10
5	8.2	99.77±0.02	99.57±0.02
6	8.9	99.81±0.10	99.80±0.10
7	9.4	99.80±0.04	99.66±0.02
8	9.8	99.88±0.03	99.72
9	10.2	99.80±0.02	99.68

TABLE VII

EFFECT OF OTHER MINERAL ACIDS ON PRECIPITATION

Amount of acid added	*Molarity of acid in final solution*	*% Phosphorus precipitated*
Sulphuric acid (s.g. 1.84)		
1 ml (1%)	0.026	100.00
1 ml (5%)	0.129	99.93
1 ml (10%)	0.258	99.95
1 ml (30%)	0.77	99.93
1 ml (50%)	1.29	88.5
1 ml conc. acid	2.58	35.5
Hydrochloric acid (s.g. 1.18)		
1 ml (1%)	0.017	99.93
1 ml (10%)	0.17	100.00
1 ml (30%)	0.50	99.93
1 ml (50%)	0.83	99.95
1 ml conc. acid	1.65	92.90
Perchloric acid (s.g. 1.66)		
1 ml (30%)	0.5	99.95
1 ml conc. acid	1.7	99.95

TABLE VIII

WEIGHTS OF PRECIPITATE OBTAINED FROM DIFFERENT ACID MEDIA

Theoretical weight expected (g)	*Amount of acid added*	*Weight of precipitate obtained (g)*
0.0353	1 ml concentrated nitric acid	0.0358
	1 ml sulphuric acid (30%)	0.0389
	1 ml hydrochloric acid (50%)	0.0366
	1 ml perchloric acid (30%)	0.0360

in the presence of these acids at 70° was obtained as in the experiments in (*b*) above (Table VIII).

(f) Precipitation of ammonium 12-molybdophosphate in the absence and in the presence of increasing amounts of nitric acid

Ammonium molybdate (35 g) was dissolved in water (900 ml) and allowed to stand for 24 h. This solution was filtered and stored in a polythene bottle.

This solution (4 ml) was added to a mixture of potassium dihydrogen phosphate (2 ml) and 0.5 μC of phosphorus-32. Different amounts of nitric acid were added at 70°, and the mixture, which was stirred at 15-min intervals, was maintained at 70° for 1 h and at room temperature for 1 h. The ammonium 12-molybdophosphate was filtered, but, on washing the precipitate with acid ammonium nitrate, the whole of the precipitate was washed through the sintered glass filter. The precipitates were therefore centrifuged and washed as in experiment (*a*). Counts were taken on the combined filtrate and washings and on the ammoniacal extract of the precipitate. The percentage of phosphorus precipitated was calculated from the corrected count-rates (Table IX).

TABLE IX

EFFECT OF NITRIC ACID ADDITION AFTER MOLYBDATE

Amount of nitric acid (s.g. 1.42) added to 2 ml phosphate solution	*Molarity of nitric acid in solution*	*% Phosphorus precipitated*
No acid	—	No precipitate formed
1 ml (0.1%)	0.002	No precipitate formed
1 ml (1%)	0.023	58.5
1 ml (10%)	0.23	99.9
1 ml (20%)	0.45	99.7
1 ml (50%)	1.14	99.8
1 ml conc. acid	2.28	99.1
2 ml conc. acid	4.56	96.6

(*g*) *Addition of ammonium nitrate before precipitation*

The experiment was repeated exactly as in the experiments in (*e*) except for the substitution of increasing amounts of ammonium nitrate for the nitric acid. The results are shown in Table X.

TABLE X

EFFECT OF AMMONIUM NITRATE ADDITION

Amount of ammonium nitrate added (g)	*Molarity of ammonium nitrate in solution*	*% Phosphorus precipitated*	
		60°	*70°*
0.04	0.083	99.97	99.94
0.08	0.17	99.97	99.99 ± 0.01
0.12	0.25	99.97	99.95 ± 0.02
0.16	0.33	99.93	99.98 ± 0.10
0.20	0.42	99.99	99.97
0.24	0.50	99.99	99.98

CONCLUSIONS

Phosphorus as phosphate can be precipitated quantitatively with the nitromolybdate reagent at any temperature in the range 50–80° provided that the reactants stand for at least 30 min at this temperature and 30 min at room temperature, and are stirred at 15-min intervals.

Gravimetric analysis of the precipitate formed at 80° shows that the composition lies between $(NH_4)_3[P(Mo_3O_{10})_4]$ and $(NH_4)_2H[P(Mo_3O_{10})_4]$ as noted by THISTLETHWAITE[1]. Analysis of the precipitate formed at 90° shows a molybdenum/phosphorus ratio greater than 12 and an ammonium content lower than that found for the compound formed at 80°. The precipitate at 90° is probably a mixture of ammonium 12-molybdophosphate and molybdic acid.

Convection currents provide adequate stirring for the mixture if it is maintained at 70° for longer than an hour and at room temperature for an hour.

Twice the stoichiometric amount of nitromolybdate reagent is sufficient to remove

99.9% of the phosphate from solution at 70°. THISTLETHWAITE[1] maintained that a 3.5 times stoichiometric amount of molybdate reagent was necessary.

The addition of concentrated nitric acid to the reaction is not detrimental to the efficient precipitation of phosphate, even when the strength of acid in the solution is raised to 10 *M*. Sulphuric acid causes the precipitate to be heavier than expected; a breakdown of the precipitate occurs in sulphuric acid or hydrochloric acid stronger than 1 *M*. Perchloric acid (0.5 and 1.7 *M*) does not interfere with the precipitation.

Nitric acid is essential to the formation of ammonium 12-molybdophosphate and should be added to the phosphate solution in the form of the nitromolybdate reagent proposed by THISTLETHWAITE[1]. When the ammonium 12-molybdophosphate is formed using the nitromolybdate reagent, the precipitate does not peptise when washed with water; peptisation of the precipitate does occur when the components, ammonium molybdate, nitric acid, and phosphate, are mixed separately. If the precipitate is to be formed in this manner, the solution should be at least 0.23 *M* with respect to nitric acid but the precipitate is so fine that it can be separated only by centrifugation.

The addition of ammonium nitrate has no effect on the efficiency of phosphate removal.

We thank D.S.I.R. for a research studentship to D.W.A.

SUMMARY

The radionuclide phosphorus-32 has been used to measure the effects of (*1*) temperature, (*2*) time of standing, (*3*) stirring, (*4*) the molybdate–phosphate ratio, (*5*) hydrochloric, sulphuric, nitric and perchloric acids, and (*6*) ammonium nitrate on the efficiency of precipitation of ammonium 12-molybdophosphate.

The precipitate is formed quantitatively after 30 min at any temperature between 50° and 80° followed by 30 min at room temperature, provided that the liquid is stirred at 15-min intervals. Twice the stoichiometric amount of nitromolybdate reagent is sufficient for quantitative precipitation. Nitric acid is essential; perchloric acid does not interfere, but hydrochloric and sulphuric acids do. Ammonium nitrate does not affect the efficiency of the precipitation.

RÉSUMÉ

Le radiophosphore-32 est utilisé pour examiner l'influence de divers facteurs sur la précipitation du phosphomolybdate d'ammonium. On peut obtenir une précipitation quantitative en observant les conditions suivantes: attendre 30 min à une température comprise entre 50 et 80°, puis 30 min à la température ordinaire, en agitant toutes les 15 min. Une quantité de nitromolybdate double de la quantité stoéchiométrique est suffisante. L'acide nitrique est nécessaire; l'acide perchlorique ne gêne pas, tandis que les acides chlorhydrique et sulfurique gênent. Le nitrate d'ammonium ne gêne pas.

ZUSAMMENFASSUNG

Die Leistungsfähigkeit der Fällung des Phosphats als Ammonium-12-molybdophosphat wurde unter Anwendung von radioaktivem Phosphor-32 untersucht. Dabei wurden folgende Einflüsse geprüft: (*1*) die Temperatur, (*2*) die Zeit zwischen Fällung und Filtration, (*3*) wiederholtes Rühren der Lösung einschliesslich Niederschlag, (*4*) das Molybdat–Phosphat-Verhältnis, (*5*) Zugabe verschiedener Mineralsäuren, (*6*) Zugabe von Ammoniumnitrat.

Die Fällung ist quantitativ, wenn bei 50–80° gefällt wird, die Lösung 30 min bei dieser Temperatur und 30 min bei Raumtemperatur steht und alle 15 min gerührt wird. Die doppelte Menge des stöchiometrisch erforderlichen Molybdats ist ausreichend. Die Zugabe von Salpetersäure ist wesentlich; Salzsäure und Schwefelsäure stören. Ammoniumnitrat beeinflusst nicht die Wirksamkeit der Fällung.

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THERMOGRAVIMETRIC INVESTIGATION OF THE ALKALI METAL DILITURATES

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Dilituric acid (5-nitrobarbituric acid) has been proposed as a precipitating agent for the thermogravimetric determination of a number of metal cations[1,2]. The precipitation by dilituric acid is rapid and offers a favorable gravimetric factor but suffers from a lack of specificity.

BERLIN AND ROBINSON[1,2] investigated the thermogravimetric determination of potassium as a diliturate and determined the thermogravimetric curves for rubidium and ammonium diliturates. This work has been extended in the present paper to include the investigation of the thermogravimetric curves of cesium, sodium, and lithium diliturates, the measurement of the solubility of cesium, lithium and rubidium diliturates in water at 24° and the thermogravimetric determination of rubidium and cesium as the diliturates.

EXPERIMENTAL AND RESULTS

Equipment

An ADAMEL recording thermobalance (Chevenard system) was used to obtain the thermolysis curves.

Coors porcelain crucibles, No. 00000, and Coors porcelain filtering crucibles, No. 00000, of 15 μ porosity were used.

Reagents

Lithium diliturate was prepared by treating a 0.2 M aqueous solution of reagent-grade lithium chloride (Mallinckrodt Chemical Works) with a slight excess of an aqueous solution of saturated dilituric acid. After cooling on ice until precipitation was essentially complete, the precipitate was collected in a fritted glass filtering crucible, washed with distilled water, then with 95% ethanol and finally dried in vacuo (water pump).

Sodium diliturate was prepared by treating a 0.1 M aqueous solution of reagent-grade sodium chloride (J. T. Baker Chemical Company) with a slight excess of 0.05 M dilituric acid in 50% ethanol. The solution was cooled and the precipitate collected in a fritted glass filtering crucible. The precipitate was washed first with distilled water, then with 95% ethanol and finally dried in vacuo (water pump).

Rubidium diliturate was prepared by treating a 0.1 M aqueous solution of C.P. rubidium chloride (Fairmount Chemical Company) with an equivalent amount of

0.05 *M* dilituric acid in 50% ethanol. The precipitate was allowed to age one day, then collected in a fritted glass filtering crucible. The precipitate was washed first with water, then with 95% ethanol and finally dried in vacuo (water pump).

Cesium diliturate was prepared by treating a 0.1 *M* aqueous solution of C.P. cesium nitrate (Fairmount Chemical Company) with an equivalent amount of 0.05 *M* dilituric acid in 50% ethanol. The precipitate was aged one day and then collected in a fritted glass filtering crucible. The precipitate was washed first with water, then with 95% ethanol and finally vacuum-dried (water pump).

The purities of the rubidium chloride and cesium nitrate were established by flame photometric analysis for sodium, potassium, rubidium and cesium using a Beckman DU flame photometer equipped with a photomultiplier tube. The compounds were found to be as pure as the distilled water used in preparing the solutions.

Nitrogen gas was dried by passing through solid calcium sulfate. The flow rate was 3 l/h.

Solutions

Saturated dilituric acid solution (0.05 *M*) in 50% ethanol was prepared from recrystallized, white-label dilituric acid (Eastman Kodak Company) as described by Berlin and Robinson[1].

Primary standard solutions of 0.0228 *M* and 0.00503 *M* rubidium were prepared from rubidium chloride which had been dried at 105°. A portion of each solution was also diluted two-fold to give 0.0114 *M* and 0.00252 *M* solutions of rubidium.

Primary standard solutions of 0.0205 *M* and 0.00480 *M* cesium were prepared from cesium nitrate dried at 150°. Previously the cesium nitrate had been investigated thermogravimetrically and found to be stable to at least 200°. From the 0.0225 *M* solution by dilution a 0.0102 *M* solution was prepared and similarly 0.00240 *M* and 0.000960 *M* solutions were prepared from the 0.00480 *M* solution by dilution.

Calibrated volumetric ware was used for measuring all volumes of solutions.

Solubilities of the alkali dilituraters

Previously the solubilities of the sodium, potassium and ammonium dilituraters at 25° were reported by Redemann and Niemann[3]. The solubilities of cesium, rubidium and lithium dilituraters in water at 24° have been determined and are reported in Table I. The solubilities were determined by saturating at room tempera-

TABLE I

SOLUBILITIES OF THE ALKALI DILITURATES

	Solubility	
	Moles/l	*Ksp*
$LiD \cdot H_2O$	$1.0 \cdot 10^{-1}$	$1.0 \cdot 10^{-2}$
$NaD \cdot H_2O$	$3.8 \cdot 10^{-2}$[a]	$1.4 \cdot 10^{-3}$
KD	$3.9 \cdot 10^{-3}$[a]	$1.5 \cdot 10^{-5}$
RbD	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-6}$
CsD	$9.3 \cdot 10^{-4}$	$8.6 \cdot 10^{-7}$

[a] As determined by Redemann and Niemann[3].

ture (24°±1°) by stirring with an excess of the salt, letting stand for several days filtering through Whatman No. 42 filter paper and then evaporating 25-ml portions of the filtrate by water pump desiccation.

The results show that with increasing atomic weight of the alkali metal the solubility of the alkali diliturate decreases. The solubilities of cesium diliturate and rubidium diliturate are sufficiently small to permit thermogravimetric determination of these cations as the diliturates.

Thermolysis curves

The thermolysis curves in Fig. 1 were obtained by heating the diliturates in No. 00000 porcelain crucibles, in an atmosphere of nitrogen flowing at a rate of 3 l/h. The weights of the samples and the corresponding rates of heating for each curve are recorded on the Fig.

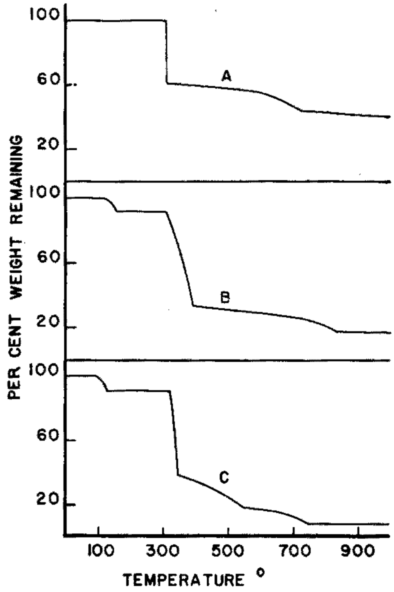

Fig. 1. Thermolysis curves of alkali diliturates: (A) cesium diliturate, 21.2 mg heated at 300°/h; (B) sodium diliturate, 28.0 mg heated at 300°/h; (C) lithium diliturate, 28.6 mg heated at 300°/h.

Cesium diliturate formed no hydrate and was stable to 310°. At 310° an extremely rapid and almost explosive decomposition took place. From 313° the decomposition was gradual to 600° where there was a slight inflection point corresponding to Cs_2CO_3. At 735° cesium peroxide (Cs_2O_2) was formed. Above 735° the cesium peroxide sublimed and no stable weight region was reached.

Sodium diliturate monohydrate showed a loss of one mole of water starting at 118° and terminating at 160°. Anhydrous sodium diliturate was stable to 308° and then began to decompose rapidly to 390° and then rather slowly to 837° with the production of sodium oxide (Na_2O). There was a slight inflection at 730° corresponding to Na_2CO_3. The sodium oxide lost weight very slightly and from the appearance of the crucible appeared to be subliming.

Lithium diliturate monohydrate showed a loss of one mole of water starting at 100° and terminating at 130° with the production of the anhydrous salt. Anhydrous lithium diliturate was stable to 325°, decomposing rapidly to about 336° and then rather slowly to 550° where an inflection point corresponding to Li_2CO_3 was indicated. Lithium carbonate decomposed slowly to 650° then more rapidly to 740° with the production of Li_2O.

Thermogravimetric analysis for rubidium

Aliquot samples (10 ml) of rubidium chloride solutions were treated with enough 0.05 *M* dilituric acid solution (50% ethanol) to give a 1:4 mole ratio of Rb:D. The precipitate was allowed to form for about 30 min at room temperature and then cooled on ice for 1 h. The precipitate was collected in a No. 00000 filtering crucible, washed with 0.01 *M* dilituric acid solution (50% ethanol), followed by 95% ethanol and then weighed after heating at 130–150°. The samples from the most dilute rubidium solution were treated with sufficient dilituric acid to give a 1:7 mole ratio excepting one which had only a 1:4 mole ratio.

TABLE II

DETERMINATION OF RUBIDIUM AS RUBIDIUM DILITURATE

RbD precipitate (mg)	*Rb taken (mg)*	*Rb found (mg)*	*Deviation (mg)*
59.0	19.4	19.6	+0.2
58.7	19.4	19.5	+0.1
58.6	19.4	19.4	0.0
58.9	19.4	19.5	+0.1
29.4	9.72	9.75	+0.03
29.3	9.72	9.72	0.00
29.4	9.72	9.75	+0.03
12.9	4.30	4.28	−0.02
13.3	4.30	4.40	+0.10
12.8	4.30	4.25	−0.05
12.9	4.30	4.28	−0.02
5.37[a]	2.15	1.78	−0.37
6.14[b]	2.15	2.04	−0.11
6.14	2.15	2.04	−0.11
6.12	2.15	2.03	−0.12

[a] 1:4 Rb:D.
[b] 1:7 Rb:D.

Table II lists the results obtained by this method. The precipitate was found to be dense and easily handled. From 19.4 to 4.30 mg rubidium per 10 ml of solution the method was accurate to 0.7%. At 2.15 mg the mole ratio of rubidium to diliturate became very important, as is indicated by the negative error of 0.37 mg for a 1:4 mole ratio compared to a 0.11 mg negative error at a mole ratio of 1:7. Samples yielding more than 60 mg of precipitates were precluded by the size of the 1.3-ml filtering crucible.

Thermogravimetric analysis for cesium

Aliquot samples (10 ml) of the cesium nitrate solutions were treated with enough 0.05 *M* dilituric acid solution (50% ethanol) to give a 1:4 mole ratio of Cs:D. The precipitate was allowed to form at room temperature for 30 min and then cooled on ice for 1 h. The precipitate was then collected in a No. 00000 filtering crucible, washed with 0.01 *M* dilituric acid solution (50% ethanol), followed by 95% ethanol and finally weighed after heating at 130–140°. The most dilute cesium solution was treated with a 1:6 mole ratio of cesium to diliturate.

TABLE III

DETERMINATION OF CESIUM AS CESIUM DILITURATE

CsD precipitate (mg)	*Cs taken (mg)*	*Cs found (mg)*	*Deviation (mg)*
62.6	27.2	27.3	+0.1
62.7	27.2	27.3	+0.1
62.4	27.2	27.2	0.0
31.6	13.6	13.8	+0.2
31.2	13.6	13.6	0.0
31.0	13.6	13.5	−0.1
31.1	13.6	13.6	0.0
14.7	6.38	6.40	+0.02
14.5	6.38	6.34	−0.04
14.7	6.38	6.42	+0.04
14.6	6.38	6.37	−0.01
7.16	3.19	3.12	−0.07
7.22	3.19	3.14	−0.05
7.35	3.19	3.20	+0.01
7.38	3.19	3.22	+0.03
2.58[a]	1.27	1.12	−0.15
2.64	1.27	1.15	−0.12
2.59	1.27	1.13	−0.14

[a] 1:6 mole ratio of Cs:D.

Table III lists the results obtained with cesium. It was found that the precipitate was dense, formed rapidly and was easily handled. In the range of 27.2 to 3.19 mg cesium per 10 ml of solution the method was found to be accurate to 0.6%. At 1.27 mg cesium even with a 1:6 mole ratio of Cs:D, the results were low by about 13 parts per hundred. Higher amounts than 27.2 mg of cesium were precluded by the capacity of the 1.3-ml filtering crucible.

SUMMARY

Thermolysis curves for lithium, sodium and cesium diliturates have been obtained. Lithium and sodium diliturates form monohydrates from aqueous solutions while potassium, rubidium, and cesium diliturates are anhydrous.

The cesium and rubidium diliturates form rapidly, are quite dense, and easily handled. Both diliturates are thermally stable to about 300°. Methods for the thermogravimetric determination of rubidium and cesium have been developed and found to be quite accurate.

RÉSUMÉ

Les courbes de thermolyse des diliturates de lithium, de sodium et de césium ont été tracées. A partir de solutions aqueuses, les diliturates de lithium et de sodium obtenus sont monohydratés, tandis que ceux de potassium, de rubidium et de césium sont anhydres. Tous ces diliturates sont thermiquement stables à environ 300°. Des méthodes de dosage thermogravimétrique ont été mises au point pour le rubidium et le césium.

ZUSAMMENFASSUNG

Es wurden Thermolysekurven für Lithium-, Natrium- und Cäsium-Diliturat gemessen. Lithium- und Natrium-Diliturat bilden Monohydrate aus wässrigen Lösungen, während Kalium-, Rhubidium- und Cäsium-Diliturat Anhydride bilden. Die Cäsium- und Rhubidium-Diliturate bilden sich schnell, sind fest und leicht zu handhaben. Beide sind bis 300° thermisch stabil. Methoden zur thermogravimetrischen Bestimmung von Rhubidium und Cäsium wurden entwickelt.

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FLUOROSULPHURIC ACID AS A TITRANT IN ALCOHOLIC SOLVENTS

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Perchloric acid has commonly been used as the acidic titrant for non-aqueous titrations because it was known as the strongest acid. However, it suffers from the defect that it is not available in a pure state and its solutions have to be prepared indirectly. Recently, PAUL *et al.*[1] have shown that fluorosulphuric acid is even stronger than perchloric acid with the added advantage that it can be easily prepared in a pure state. On this basis, fluorosulphuric acid has already been developed as an acidic titrant for titrations in acetic acid; organic bases, amino acids, alkaloids, acetates[2], etc., have been determined.

Methanol and ethanol have long been used as media for non-aqueous titrations and the theoretical as well as practical aspects of the subject are fully understood[3-6]. The use of glycol and glycolic mixtures as solvents for non-aqueous titrations for the estimation of basic substances is comparatively recent[7]. In the recent editions of the British Pharmacopoeia (1958), British Pharmaceutical Codex (1959), United States Pharmacopoeia XV and International Pharmacopoeia, these solvents are recommended as media for many non-aqueous titrations with perchloric acid as the acidic titrant.

In the present work, fluorosulphuric acid was employed as an acidic titrant in these alcoholic media for the determination of bases. Potentiometric and visual methods were used for the detection of the end-points. Besides the pure alcohols, mixtures of glycol with methanol, isopropanol, acetone or chloroform were examined as the solvents.

EXPERIMENTAL

Reagents

Methanol. Methanol (B.D.H. Ltd.) containing a maximum of 0.01% water was used after distilling over magnesium and a small amount of iodine (b.p. 64.5° at 740 mm).

Ethanol. Anhydrous ethanol was prepared as suggested by VOGEL[8] and was finally distilled over magnesium and a little iodine (b.p. 74.5° at 740 mm).

Isopropanol. Commercial isopropanol was refluxed over oxalic acid to remove any basic impurities and then refluxed with anhydrous calcium oxide and distilled. It was further distilled over sodium and finally over magnesium and a little iodine (b.p. 80.0° at 740 mm).

All the monohydric alcohols were found to contain less than 0.01% water.

Glycol. Ethylene glycol (B.D.H. Ltd.) was kept over anhydrous sodium sulphate for 24 h, decanted and distilled in vacuum. Only the middle fractions were used in the present work.

Acetone. Anhydrous acetone (AnalaR, B.D.H. Ltd.) was prepared as suggested by VOGEL[8] (b.p. 55.5–56° at 740 mm).

Chloroform. Chloroform (G. R.; E. Merck) was kept over anhydrous calcium chloride (A.R.) for 24 h and then distilled through a long column (b.p. 60.5° at 740 mm).

Mixed solvents. Mixtures of methanol, isopropanol and acetone with ethylene glycol were prepared in 1 : 1 volume ratios. Chloroform was found to be only partially miscible with ethylene glycol in 1 : 1 (v/v) mixtures; the addition of a few drops of isobutanol made the mixture homogeneous, and this homogeneous solution was used.

Fluorosulphuric acid. This was prepared and purified as previously suggested[1]; only the fraction distilling between 161–2° was used in the present work.

Bases. Bases were purified either by distillation or by crystallisation[1,2].

Much heat was produced on the addition of fluorosulphuric acid to the solvents; the solvents were therefore cooled when solutions of the acid were prepared.

In potentiometric titrations a quinhydrone electrode was employed as the indicator electrode with a saturated calomel electrode as the reference electrode. All the equipment and procedure were the same as mentioned earlier[1].

RESULTS AND DISCUSSION

In order to elucidate the nature of fluorosulphuric acid solutions in these solvents,

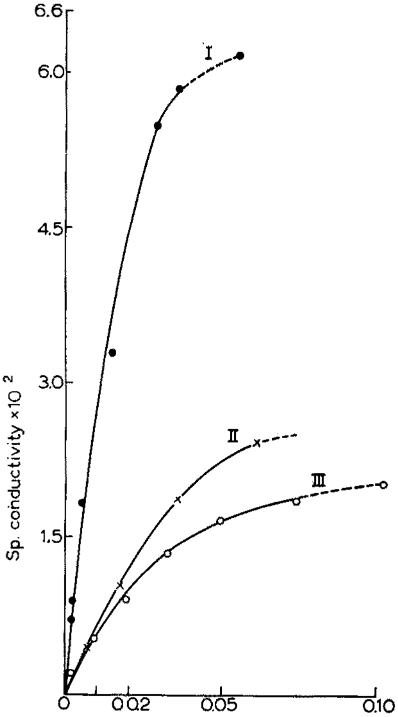

Fig. 1. Conductivity of fluorosulphuric acid at 20° in: (I) methanol; (II) glycol; (III) ethanol.

the specific conductivities were studied. The conductivities in methanol, ethanol and pure ethylene glycol were determined at various concentrations (Fig. 1). The conductivities of solutions containing higher concentrations of fluorosulphuric acid could not be determined owing to the formation of insoluble compounds, which made the conductivities almost constant. These alcohols in the pure state have a very low conductivity (methanol $2.2 \cdot 10^{-7}$/ohm/cm; ethanol $1.35 \cdot 10^{-9}$/ohm/cm; ethylene glycol $3.0 \cdot 10^{-7}$/ohm/cm)[9]. The conductivity of fluorosulphuric acid in the pure state is $2.2 \cdot 10^{-4}$/ohm/cm[10]. If there were no reaction of fluorosulphuric acid with the alcohols resulting in the formation of ions, *i.e.* if the dissolution were a simple process of solution, the specific conductivity of $< 0.1\ M$ solutions (HSO_3F/solvent) could not be in the range of $0–6 \cdot 10^{-2}$. The high conductivity is surprising, being even higher than that of the pure acid; it indicates a reaction between the alcohols and the acid which results in the formation of a compound which is even more ionic than the acid itself. The auto-ionisation of alcohols is known[11] to proceed as follows:

$$2\ ROH \rightleftharpoons RO^- + (ROH_2)^+$$

and therefore the nature of these fluorosulphuric acid solutions can be represented as

$$ROH + HSO_3F \rightarrow (ROH \cdot HSO_3F) \rightleftharpoons ROH_2^+ + SO_3F^-$$

In Fig. 2 the equivalent conductance of fluorosulphuric acid in different alcohols is plotted against the square root of the concentration. Although the concentration range studied is not very low, the values of the equivalent conductivity are fairly high. The shape of the curves, however, indicates that ionisation in solution is far from complete, as would be expected with solvents of comparatively low dielectric constant (*e.g.* methanol 32.63)[11].

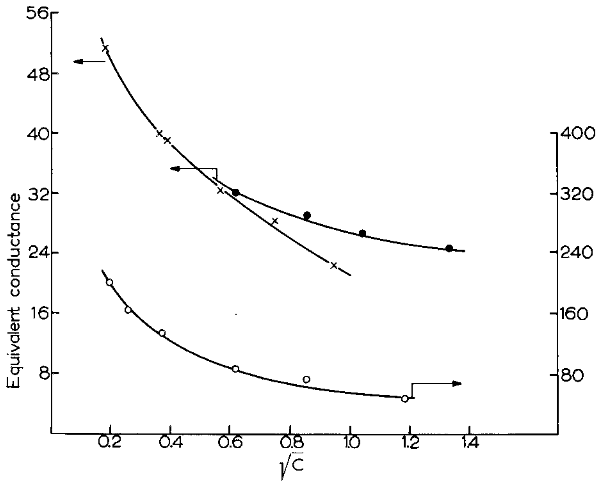

Fig. 2. Equivalent conductance of fluorosulphuric acid in alcohols at 20°: — × — × -- ethanol; —●—●— ethylene glycol; —○—○— methanol.

Figure 3 shows the potentiometric curves obtained for various bases (sodium formate, piperidine, triethylamine, *n*-butylamine, aniline, benzylamine, morpholine and α-picoline) on titration with fluorosulphuric acid in methanol. The titration

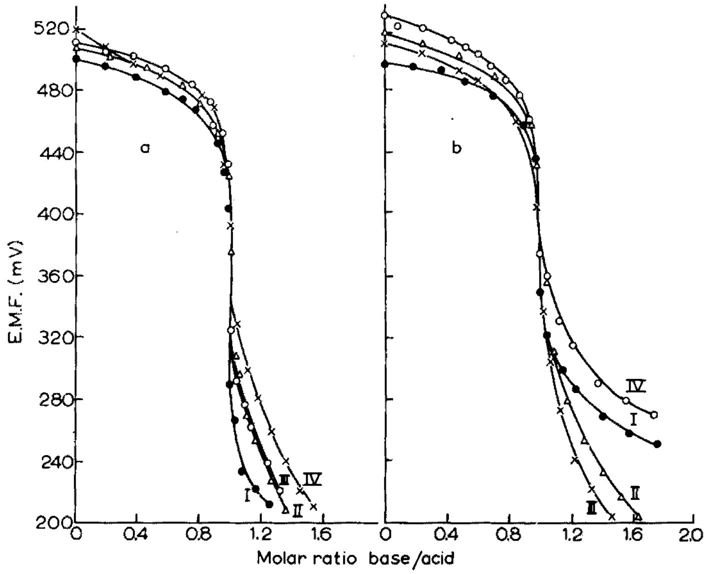

Fig. 3. Potentiometric titrations of bases with fluorosulphuric acid in methanol: (a) I, sodium formate; II, piperidine; III, triethylamine; IV, *n*-butylamine; (b) I, aniline; II, benzylamine; III, morpholine; IV, α-picoline.

curves are quite satisfactory and the experimental results agree very well with the expected theoretical values. Since the auto-ionisation of methanol is well established, the solutions of tertiary bases (B) may be represented as

$$B + CH_3OH \rightleftharpoons BH^+ + CH_3O^-$$

The neutralisation of the bases with fluorosulphuric acid may therefore be represented as

$$BH^+ + CH_3O^- + (CH_3OH_2)^+ + SO_3F^- \rightarrow 2\ CH_3OH + BH^+\ SO_3F^-$$

Sodium formate acts as a base in view of the fact that formic acid is a much weaker acid than fluorosulphuric acid in methanol.

Potentiometric titrations of organic bases such as benzylamine, morpholine, triethylamine, were also carried out in pure ethanol or ethylene glycol using fluorosulphuric acid as the titrant. The titrations were quite successful but these two solvents were not as good as methanol. Pure ethylene glycol suffers from an additional drawback due to its high viscosity; to avoid a very large drainage error, a very long time had to be allowed between two successive additions. However, its mixtures with methanol, isopropanol and acetone in the ratio of 1 : 1 by volume combined a high solvent power with low viscosity and were found to be quite suitable for titrations with fluorosulphuric acid. In Fig. 4 the potentiometric titration curves of a few bases with fluorosulphuric acid in ethylene glycol–methanol mixture are given and it is clear that the titrations were quite successful. Titrations were also quite successful in the other two mixed solvents. In ethylene glycol–isopropanol mixture, sodium acetate was successfully titrated with fluorosulphuric acid, which indicates the great difference in the strengths of acetic acid and fluorosulphuric acid in this solvent.

Since the solutions in the various solvents were of approximately the same strength, in a qualitative way the potential drop at the neutralisation point would indicate the suitability of the solvents. Thus methanol and mixtures of ethylene glycol with methanol were most suitable for the simple bases tried, though the titrations were quite successful in all the other media. PALIT[7] has used mixtures of ethylene glycol with acetone, isopropanol and butanol and has recommended the first two mixtures as most suitable. However, the present work indicates the ethylene glycol–methanol mixture to be even better than the two glycolic mixtures recommended by PALIT and co-workers.

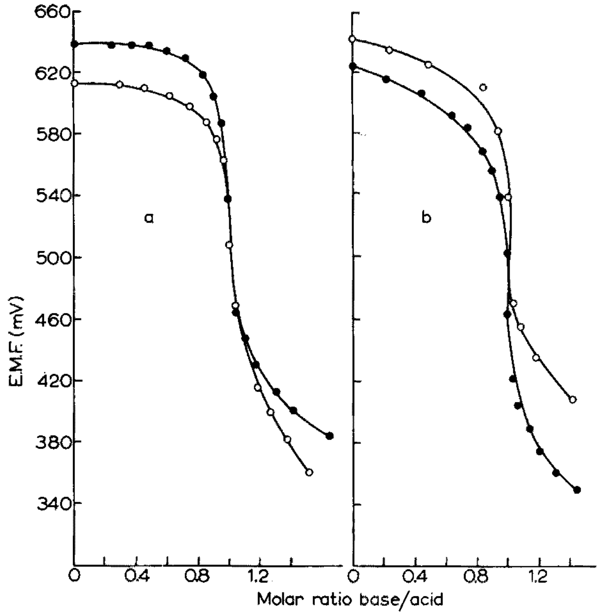

Fig. 4. Potentiometric titrations of bases with fluorosulphuric acid in glycol–methanol mixture: (a) —○—○— benzylamine; —●—●— aniline; (b) —○—○— *n*-butylamine; —●—●— triethylamine.

Dimethyl yellow, methyl orange and methyl red are some of the azo compounds which have been used as indicators in aqueous solution in the acidic pH range, the colour changing from red or pink to yellow as the pH increases. In anhydrous alcoholic media the colour changes are even more pronounced. These indicators have already been used in alcoholic media to determine end-points[7]. They were tested for the present series of titrations with fluorosulphuric acid as the titrant in methanolic medium and in mixtures of ethylene glycol with methanol, isopropanol and acetone; titrations were also carried out in a glycol–chloroform mixture which was made homogeneous by the addition of a few drops of isobutanol. The reversible behaviour of these indicators was confirmed for methanol and glycol–methanol mixture. The results of the titrations in these two media are given in Tables I and II, whence it is evident that the results are within the normal limits of error. Titrations in the other glycolic media mentioned earlier were also quite successful. It is thus clear that fluorosulphuric acid can be safely used in place of perchloric acid for the titration of different basic substances.

TABLE I

VISUAL TITRATIONS OF BASES WITH FLUOROSULPHURIC ACID AS TITRANT IN METHANOL

Base	Weight of sample (g)	Concn. of titrant (g. equiv./l)	g. equiv. titrated · 10^5			
			Theoretical	Experimental		
				Dimethyl yellow	Methyl orange	Methyl red
Dimethylaniline	0.0621	0.1251	51.32	51.29	51.55	51.29
α-Picoline	0.0409	0.1251	43.98	43.79	43.79	43.79
Isoquinoline	0.0800	0.1251	62.05	61.92	61.92	62.55
Pyridine	0.0538	0.1251	68.08	67.55	68.05	68.05
n-Butylamine	0.0360	0.1251	49.31	49.41	49.41	49.03
Diethylaniline	0.0731	0.1251	49.03	48.79	49.79	48.79
		Visual titrations of fluorosulphuric acid with bases as titrants in methanol				
Dimethylaniline	0.0626	0.1027	62.55	62.61	62.61	
α-Picoline	0.0626	0.0879	62.55	62.08	62.44	
Isoquinoline	0.0626	0.1241	62.55	62.30	62.67	
Pyridine	0.0625	0.1362	62.55	62.63	62.63	
n-Butylamine	0.0625	0.0985	62.55	62.95	62.27	

TABLE II

VISUAL TITRATIONS OF BASES WITH FLUOROSULPHURIC ACID AS TITRANT IN GLYCOL–METHANOL MIXTURE

Base	Weight of sample (g)	Concn. of titrant (g. equiv./l)	g. equiv. titrated · 10^5			
			Theoretical	Experimental		
				Methyl orange	Methyl red	Dimethyl yellow
Dimethylaniline	0.0600	0.1667	49.58	49.18	50.01	50.01
Aniline	0.1161	0.1667	124.73	125.02	125.02	125.02
Pyridine	0.0867	0.1667	109.63	110.02	108.69	110.02
Quinoline	0.0654	0.1667	50.69	50.34	50.34	50.34
		Visual titrations of fluorosulphuric acid with bases as titrants in glycol–methanol mixture				
Triethylamine	0.0769	0.2121	76.90	77.20	77.02	77.40
Benzylamine	0.0769	0.4701	76.90	77.40	76.02	77.10
Aniline	0.0769	0.2240	76.90	77.30	76.90	77.28
n-Butylamine	0.0769	0.4486	76.90	77.52	77.32	77.30

SUMMARY

Fluorosulphuric acid gives highly conducting solutions in alcohols and alcoholic mixtures. Solutions in methanol or in ethylene glycol–methanol give the best results for the direct titration of organic bases, although other alcohols are also satisfactory. Potentiometric and visual methods of end-point detection are suitable.

RÉSUMÉ

Les auteurs proposent l'utilisation de l'acide fluorosulfonique pour le titrage direct de bases organiques, en milieu alcoolique. Les solutions dans le méthanol ou dans le mélange éthylèneglycol –méthanol ont donné les résultats les meilleurs. Le point final peut être décelé soit par potentiométrie, soit par méthodes visuelles.

ZUSAMMENFASSUNG

Es wurde die Verwendbarkeit von Fluorsulfonsäure (HSO_3F) zur Titration von organischen Basen in alkoholischen Lösungen untersucht. Neben anderen geeigneten Lösungsmitteln ergaben Methanol oder Äthylenglykol–Methanol die besten Ergebnisse. Potentiometrische und visuelle Endpunktsmethoden sind anwendbar.

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THE APPLICATION OF ISOTOPIC DILUTION ANALYSIS TO THE FLUORIMETRIC DETERMINATION OF SELENIUM IN PLANT MATERIAL

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Interest in the determination of selenium in plant material stems from the work of SCHWARZ AND FOLTZ[1] which showed that trace amounts of selenium are of nutritional benefit. The nutritional aspects of selenium in biological material were recently reviewed by KING[2] who also pointed out the need for a better method of analysis. Difficulties in the analysis of selenium in plant material come about from loss of selenium in the first stages of the analysis in which the sample is decomposed, and from interference effects by foreign ions in the sample which prevent proper color development.

TAUSSKY and co-workers[3] as well as GUTENMANN AND LISK[4] used an oxygen-flask combustion to prepare biological samples for selenium analysis and then determined selenium spectrophotometrically by extracting the piazselenol formed with selenium and the aromatic *o*-diamine, 3,3′-diaminobenzidine. WATKINSON[5] employed this same reagent for a fluorimetric determination of selenium. The use of this reagent in selenium analysis has been recently reviewed[6]. Studies of other *o*-aromatic diamines[7,8] have shown that 2,3-diaminonaphthalene (DAN) is a more sensitive reagent. GORSUCH[9] incorporated radioactive selenium in a study of the "wet oxidation" of cocoa and showed the great dependency on the reaction conditions for the recovery of selenium in this method of sample preparation.

Reported herein is a study on the determination of micro amounts of selenium in plant material in which the samples are prepared by oxygen-flask combustion and their selenium content is determined fluorimetrically with DAN. Compensation for loss of selenium throughout the analytical procedure is made by the incorporation of radioactive selenium into the analytical scheme. Also included is further information relating to the reaction between DAN and selenium, the structure of piazselenols, and the reaction of additional aromatic *o*-diamines with selenium.

EXPERIMENTAL

Apparatus and reagents

Optical measurements were performed with a Coleman Model 12 C Photofluorimeter using as primary filters the combination of Corning Glass Co. 7-60 and 0-52 filters, and an Eastman Kodak Wratten K2 secondary filter.

Radioactivity measurements were made with a Nuclear Chicago Model 151A scaler using a 3/8″ well-type scintillation probe with a sodium iodide crystal.

2,3-Diaminonaphthalene solution was prepared by dissolving 50 mg of purified material in 100 ml of 0.10 *N* hydrochloric acid. The commercial 2,3-diaminonaphthalene (Aldrich Chemical Co., Milwaukee, Wisconsin) was purified by forming a saturated solution of the amine in 5 *N* hydrochloric acid and then adding saturated sodium hydroxide solution dropwise to reform the amine. The amine was filtered and washed with water until the pH of the filtrate was between 5–7; the amine was then dried at 100°. Observed melting points 190–191°; literature 191–194°. The amine was stored under refrigeration and was repurified whenever the crystals were yellowish in appearance.

Standard selenium solution containing 1.00 mg of selenium per ml was prepared by dissolving 1.6336 g of selenous acid (H_2SeO_3) in 1 l of water. Other solutions were prepared by appropriate dilution of this stock solution.

Radioactive selenium-75 solution was prepared by adding 100 µl of the original 1 mC/2 ml selenous acid solution (Oak Ridge National Laboratory) to 100 ml of 1.2 *N* hydrochloric acid.

Spectrograde cyclohexane was used.

PROCEDURE

For the determination of selenium in plant material, combustion sample holders were cut from No. 589 black ribbon Schleicher and Schüll filter paper, using a Fisher Scientific Co. # 13–304 combustion sample holder as a pattern. A series of sample holders were placed on watchglasses and 50 µl of radioactive selenium solution were placed upon each sample holder using a 0.25-ml tuberculin syringe with a 26-gauge needle. A pipetting stop was fastened to the syringe. The sample holders were allowed to dry overnight in air and then variable amounts (from 0 to 100 µl) of 5 p.p.m. selenium solution were placed upon the sample holders respectively and the sample holders were again allowed to dry. A 100-mg sample of plant material was wrapped into the treated sample holder, which was then inserted into the combustion head. To the combustion flask were added 30 ml of water, and prior to ignition the outside of the filter paper was wetted with 2 drops of cyclohexane. After combustion, the flask was shaken manually for 5 min to dissolve the products from the combustion; the contents of the flask were transferred to a 150-ml beaker and the combustion flask was rinsed with 10 ml of water which was then added to the previous contents of the flask. Then 1 ml of freshly prepared potassium persulfate solution (0.1 g/l) was added, and the contents of the beaker were boiled for 5 min. After the solution had cooled to room temperature, 1 ml of 0.1 *M* EDTA solution was added and the acidity was adjusted to pH 2.0 using either hydrochloric acid or sodium hydroxide solution; then 0.5 ml of DAN solution was added and the mixture was allowed to stand for 2 h. A 3/8″ × 3″ Lusteroid tube (Atomic Accessories, Valley Stream, N.Y.) was filled with a portion of the sample and a count was made for 4000 counts. The contents of the beaker and the Lusteroid tube were transferred to a 120-ml separatory funnel and the sample was extracted with 10 ml of cyclohexane by shaking for 5 min. The layers were separated, and the aqueous layer was re-extracted with 5 ml of cyclohexane, by shaking again for 5 min. The organic extracts were combined and the fluorescence of the organic layer was measured. Then a portion of the organic layer was transferred to another Lusteroid tube and counted for 1000 counts.

Two calibration curves were prepared by adding to a series of beakers which contained 40 ml of water and 50 µl of radioactive selenium solution, from 0 to 100 µl of 5 p.p.m. selenium solution respectively; 1 ml of potassium persulfate solution was added, and then the procedure was continued with the boiling of the samples and all steps described above. A sample containing no selenium was used to set the zero reading of the fluorimeter and the sample of highest concentration containing either 0.3 or 0.5 µg of selenium was used to set the instrument at 85% fluorescence. This was done to prepare calibration curves to cover the range of selenium concentration present in actual samples. Dilute solutions of quinine sulfate were prepared to cover this same range of fluorescence intensities, and these quinine sulfate solutions were then employed as "reference" standards for daily use in retaining the instrument settings.

The average specific activity of the aqueous phase and of the organic phase of the standards which were used to prepare the calibration curve was calculated. To correct for loss of selenium in an unknown sample, the value of the concentration of selenium measured from the calibration curve was multiplied by the correction factor obtained as follows:

$$\text{Correction factor} = \frac{\text{activity of sample in aqueous phase}}{\text{activity of standard in aqueous phase}} \times \frac{\text{activity of standard in organic phase}}{\text{activity of sample in organic phase}}$$

(The average specific activity of the standard sample in the aqueous phase was 50 counts/min/ml and the average specific activity of the organic phase after extraction was 80 counts/min/ml.)

Results on the analysis of the plant samples are reported in Table I.

TABLE I

RESULTS OF SELENIUM ANALYSIS

Sample	*Selenium*			*Average Se content (p.p.m.)*
	Added (µg)	*Found (µg)*[a]	*Present (µg)*	
Oats	None	0.047	−0.063	
(0.100 g)	0.10	0.234	0.034	None
	0.20	0.276	−0.024	
Cornflakes	None	0.118	0.018	
(0.100 g)	0.10	0.248	0.048	0.44
	0.30	0.342	0.068	
	0.50	0.780	0.180	
Rice	None	0.15	0.05	
(0.100 g)	0.10	0.22	0.02	0.20
	0.20	0.31	0.01	
	0.30	0.40	0.00	
Grass-seeds	None	0.305	0.205	
(0.050 g)	0.10	0.335	0.135	6.60
	0.20	0.880	0.580	
	0.30	0.770	0.370	

[a] Before subtracting 0.10 µg for the average selenium content of the filter paper.

RESULTS AND DISCUSSION

Extraction conditions and interference study

Previous work[8] has shown that the maximum color development takes place at pH 2 after standing for 2 h and that in toluene the maximum intensity for fluorescent radiation is at an excitation wavelength of 390 mμ and fluorescent wavelength of 540 mμ. In the course of the previous work measurements were made with an Aminco–Bowman Spectrophotofluorimeter. As that instrument was not available for present work, measurements were limited to the Coleman 12 C photofluorimeter. This instrument showed a very high blank reading with toluene and impure DAN. Consequently, other solvents were tested as extracting agents by measuring the difference in the fluorescence between the reagent (DAN) and its piazselenol. Values for the per cent piazselenol extracted were obtained by measuring the specific activity of the isotope in the organic phase and aqueous phase after extraction. The data are presented in Table II.

TABLE II

STUDY OF DIFFERENT SOLVENTS AS EXTRACTING AGENTS[a]

Solvent	*Se added (μg)*	*Fluorescence*	*% Extracted*
Carbon tetrachloride	0.0	5	
	5.0	71	19.4
Chloroform	0.0	49	
	5.0	51	20.0
Ethylenedichloride	0.0	35	
	5.0	62	20.0
Toluene	0.0	20	
	0.25	25	
	0.50	53	
	1.00	100	22.2
Cyclohexane	0.0	6	
	0.25	30	
	0.50	55	
	1.00	100	23.8

[a] 40 ml of aqueous solution at pH 2 which contained the indicated amount of selenium was extracted for 1 min with 10 ml of solvent.

The above results confirmed the work of PARKER AND HARVEY[7] that cyclohexane is a better extracting solvent than toluene and that purified DAN is necessary to minimize the blank reading. Because of the availability of spectrograde cyclohexane it was chosen in preference to decalin.

The effect of the pH of the aqueous layer prior to extraction with cyclohexane was measured and the results are presented in Fig. 1. Data on per cent extraction as a function of extracting time are reported in Table III.

The use of ion-exchange resins in the procedure was impossible with the photofluorimeter used in this study. Trace amounts of resin monomer were carried along in the procedure and the fluorescence of the monomer could not be filtered out.

Consequently a study of the effect of foreign ions in the procedure was made in which the radioactive selenium isotope was used to correct for interferences. For this study 2 ml of 0.01 *M* foreign ion solution was added to 40 ml of water containing 0.2 μg of selenium and 50 μl of the radioactive selenium solution. The results are listed in Table IV. Of 20 metallic ions tested, major interference was observed from chromium(III), antimony(III) and tin(IV). Radioactivity measurements showed that the interference of tin was due to a reduction of selenium, while antimony and chromium enhanced the fluorescence.

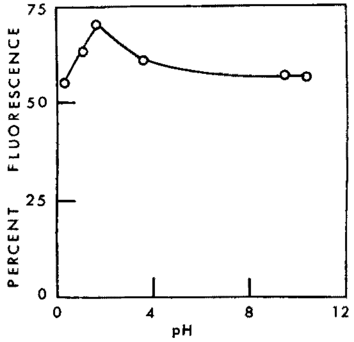


Fig. 1. Effect of pH on extraction.

TABLE III

PER CENT PIAZSELENOL EXTRACTED AS FUNCTION OF EXTRACTION TIME

First extraction: 10 ml cyclohexane					*Second extraction: 5 ml cyclohexane*	*Combined 15 ml cyclohexane extract*
Time of extraction (min)	1	3	5	10	5	—
% Extracted	23.8	28.2	29.0	29.0	5.2	34.0

Combustion conditions

Gutenmann and Lisk[4] employed a spectrophotometric determination to detect the amount of selenium in oats after oxygen-flask combustion. Because of the lower sensitivity of this method compared to a fluorimetric determination, they required 1-g samples compared to 0.1 g in our procedure. Smaller sample concentrations are desirable as in larger samples complete combustion is more difficult. We observed that the conditions of combustion were not reproducible. This was ascertained by using as combustion samples filter paper which contained only radioactive selenium and standard selenium solution. A comparison of the specific activity of the aqueous layer measured directly after combustion against the specific activity of the aqueous layer of standard solutions, showed that the recovery was random and at times only 65% of the selenium added was recovered. This variability can be corrected by isotopic dilution techniques. Measurements of the ratios of the specific activity of the

TABLE IV

FOREIGN ION EFFECT

(Selenium concentration 0.20 μg)

Ion	*Specific activity of aqueous phase prior to extraction (counts/min/ml)*	*Specific activity of organic phase after extraction (counts/min/ml)*	*Correction factor*	*Selenium concentration (μg)*	
				Calibration curve	*Corrected by factor*
Al(III)	53.2	82.5	1.03	0.24	0.25
Ba(II)	36.2	88.5	0.65	0.43	0.28
Bi(III)	42.5	73.5	0.93	0.26	0.24
Ca(II)	40.0	73.5	0.88	0.22	0.19
Cd(II)	53.2	82.5	1.03	0.24	0.25
Co(II)	44.5	109.0	0.65	0.40	0.26
Cr(III)	39.4	105.0	1.40	0.38	0.53
Cu(II)	36.7	98.0	1.18	0.08	0.09
Fe(III)	47.6	57.2	1.34	0.14	0.18
Hg(II)	52.0	73.1	1.13	0.24	0.27
K(I)	53.2	82.5	1.03	0.24	0.25
Mg(II)	39.0	88.5	0.71	0.48	0.34
Mn(II)	40.0	73.2	0.89	0.23	0.20
Na(I)	53.2	82.5	1.03	0.24	0.25
Ni(II)	71.5	103.0	1.11	0.24	0.27
Pb(II)	53.2	82.5	1.03	0.24	0.25
Sn(IV)	41.0	—	—	0.15	—
Sr(II)	37.7	63.0	0.96	0.22	0.21
Sb(III)	35.2	72.0	0.79	0.55	0.44
Zn(II)	53.2	82.5	1.03	0.24	0.25

organic and aqueous layers showed that the extraction step is more reproducible than the combustion step (Table V).

A variable introduced into the procedure is the selenium content of the filter paper used to prepare the sample holders for the combustion. The selenium content of the filter paper was about 0.1 μg, which necessitated a high blank subtraction in the combustion analysis. Different combustion materials were tried such as dialysis casing, acetate paper, gelatin capsules and different makes of filter paper. The Schleicher and Schüll 589 paper appeared most uniform and was used throughout for the combustion. This paper showed an average selenium content of 0.1 μg which

TABLE V

REPRODUCIBILITY OF COMBUSTION AND EXTRACTION

Selenium added (μg)	*% Recovered in aqueous solution after combustion*	*% Extracted from the aqueous solution*
None	65	18.5
0.10	75	19.5
0.20	80	16.7
0.30	100	19.2
0.50	79	21.2

was subtracted from all samples. An exhaustive study on the selenium content of filter paper was recently reported by West and Cimerman[10].

At one time diluted solutions of the isotope were stored in Lusteroid tubes. After several days of storage, the specific activity of the organic layer of samples prepared in the same manner as those of the calibration curve, was lower than the specific activity of the organic layer of similarly treated samples which went through the flask combustion. Yet, the specific activity of the aqueous solution was at its normal value in both cases. This was probably due to a partial reduction of selenium(IV) in the Lusteroid tube. Only selenium(IV) reacts with aromatic *o*-diamines to form the piazselenols, and during the combustion any reduced selenium was reoxidized to the selenium(IV) state. Reduction of the isotope solution was not observed if the isotope was stored in glass containers; consequently, all solutions of the isotope were stored in glass bottles.

EDTA was employed in the procedure as a masking agent. Potassium persulfate was added as an oxidizing agent to assure that all selenium was in the tetravalent state and that any traces of nitrite were oxidized to nitrate. The interference of nitrite but not nitrate has been reported previously[8].

Accuracy and precision

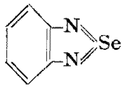
The recovery of selenium in the samples tested was satisfactory. Based upon the interference tests in Table IV, the standard deviation for the determination of selenium was 0.04 μg. The precision and accuracy of the method does not appear to be limited by the chemical steps in the procedure, but rather upon the quality of the fluorescent readings. With the instrument which was available, measurements could not be made with sufficiently monochromatic radiation to attain ultimate accuracy.

Reaction of selenium with aromatic o*-diamines*

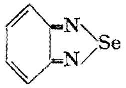
The reaction of selenium with 2,3-diaminonaphthalene[8] and 3,3′-diaminobenzidine[11] is quite pH-dependent. Preliminary kinetic investigations showed that the rate of reaction is dependent upon the amine being protonated (a favorable condition at low pH) and upon the biselenite ion concentration (a favorable effect at high pH). Other aromatic *o*-diamines were prepared; for these amines the optimum rate of reaction also occurred in the acid range (pH 1–3). The fluorescent and absorption spectra were measured for those compounds which showed the greatest promise as analytical reagents. The molar absorptivities and relative degree of fluorescence are summarized in Table VI. The fluorescent spectra are presented in Fig. 2.

The reaction of selenium with aromatic *o*-diamines (*e.g.* 1,2-diaminobenzene) could produce either a benzenoid structure or a quinoid structure for the piazselenol.

Benzenoid structure



Quinoid structure



The quinoid structure was proposed by Luzzati[12], from X-ray crystallographic measurements. Although nuclear magnetic resonance spectra of the piazselenols of 2,3-diaminonaphthalene and 1,2-diamino-4,5-dichlorobenzene were not conclusive in

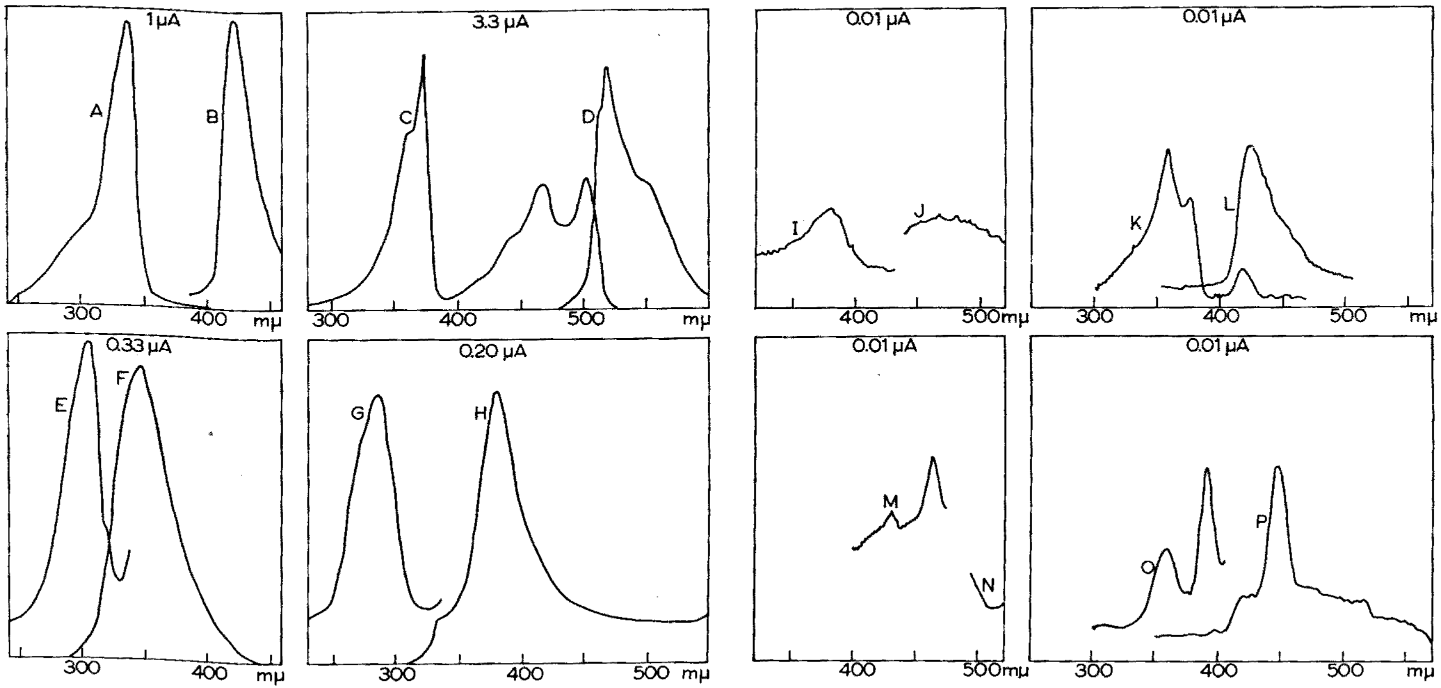
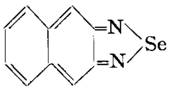
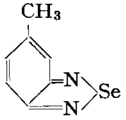
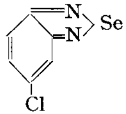
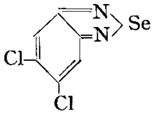


Fig. 2. Fluorescence spectra; wavelength (mμ) *vs.* fluorescence, arbitrary units, full scale, μA. (A) Excitation spectrum, 2,3-diaminonaphthalene; (B) fluorescence spectrum, 2,3-diaminonaphthalene; (C) excitation spectrum, 2,1,3-naphtho(2,3-c)selenadiazole; (D) fluorescence spectrum, 2,1,3-naphtho(2,3-c)selenadiazole; (E) excitation spectrum, 1-methyl-3,4-diaminobenzene; (F) fluorescence spectrum, 1-methyl-3,4-diaminobenzene; (G) excitation spectrum, 6-methyl-2,1,3-benzo(c)selenadiazole; (H) fluorescence spectrum, 6-methyl-2,1,3-benzo(c)-selenadiazole; (I) excitation spectrum, 1,2-diamino-4,5-dichlorobenzene; (J) fluorescence spectrum, 1,2-diamino-4,5-dichlorobenzene; (K) excitation spectrum, 5,6-dichloro-2,1,3-benzo(c)-selenadiazole; (L) fluorescence spectrum, 5,6-dichloro-2,1,3-benzo(c)selenadiazole; (M) excitation spectrum, 4-chloro-1,2-diaminobenzene; (N) fluorescence spectrum, 4-chloro-1,2-diaminobenzene; (O) excitation spectrum, 6-chloro-2,1,3-benzo(c)selenadiazole; (P) fluorescence spectrum, 6-chloro-2,1 3-benzo(c)selenadiazole.

COMPARISON OF OPTICAL PROPERTIES

Compound	*Purification procedure*	*Melting point (°)*		*Molar absorptivity*[a]	*Fluorescence*		
		Observed	*Literature*		*Relative intensity*	*Fluorescence wavelength*	*Excitation wavelength*
2,3-Diaminonaphthalene	[b]	190–191	190–194	135000 (245 mμ)	88	423	336
2,1,3-Naphtho(2,3-c)-selenadiazole 	[c]	270 dec.	290 dec.	41000 (378 mμ)	250.8	520	377
1-Methyl-3,4-diaminobenzene	[b]	82–83	88	52000 (220 mμ)	30.4	342	305
6-Methyl-2,1,3-benzo(c)selandiazole 	[c]	64	—	25000 (335 mμ)	1.7	383	291
4-Chloro-1,2-diaminobenzene	[b]	69–70	72	140000 (280 mμ)	None	492	492
6-Chloro-2,1,3-benzo(c)-selenadiazole 	[c]	117–119	—	49000 (340 mμ)	0.62	448	400
1,2-Diamino-4,5-dichlorobenzene	[b]	159–161	162–164	123000 (218 mμ)	0.28	478	375
5,6-Dichloro-2,1,3-benzo(c)-selenadiazole 	[c]	212–214	210	55000 (350 mμ)	0.51	430	360

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[a] Compound dissolved in cyclohexane

[b] Purified by forming the hydrochloride of the compound and re-precipitating the compound with sodium hydroxide

[c] Recrystallized from petroleum ether

showing that in these compounds the piazselenol also exists in the quinoid form, the quinoid structure was confirmed by infrared spectra.

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SUMMARY

A method has been developed for the fluorimetric determination of selenium in plant material using the reagent 2,3-diaminonaphthalene. Oxygen-flask combustion is used to oxidize plant material. Isotopic dilution techniques are incorporated to account for loss in different stages of the procedure. Measurements are also included on the suitability of several other amines as reagents for selenium.

RÉSUMÉ

Les auteurs ont développé une méthode pour le dosage fluorométrique du sélénium dans les plantes, après destruction de la substance dans l'oxygène, en utilisant le diamino-2,3-naphtalène comme réactif. Ils ont appliqué des techniques par dilution isotopique pour évaluer les pertes dans les différents stades du procédé. Plusieurs autres amines ont été également examinées, en tant que réactifs du sélénium.

ZUSAMMENFASSUNG

Es wurde eine Methode für die fluorimetrische Bestimmung von Selen im Pflanzenmaterial entwickelt. Die Substanz wurde im Schöniger-Kolben verbrannt und 2,3-Diaminonaphthalin als Reagenz benutzt. Mit Hilfe der Isotopenverdünnungstechnik wurde der Verlust bei den verschiedenen Verfahrensstufen festgestellt. Verschiedene andere Amine wurden auf ihre Brauchbarkeit als Reagenz für Selen geprüft.

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THE DETERMINATION OF MANGANESE IN IRON AND STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Manganese is an important residual and alloying element in iron and steel and satisfactory quantitative procedures have been established for this determination. The majority of solution techniques are based on the oxidation of Mn^{2+} to Mn^{7+} with ammonium persulphate[1,2], sodium bismuthate[1], potassium periodate[1,3], perchloric acid[4] or silver(II)[5] and subsequent determination by spectrophotometry[1,2] or by titration with arsenic(III)[1], iron(II)[1,2,4,5] or mercury(I)[6]. Other techniques which are used, include emission spectroscopy, X-ray fluorescence[7], flame emission photometry[8], potentiometry[9] and activation analysis[10]. Atomic absorption spectrophotometry has been applied to the determination of manganese in agricultural materials[11] and GIDLEY[12] and MENZIES[13] have demonstrated potential applications to metallurgical materials. The present study has shown atomic absorption spectrophotometry to be a suitable method for the determination of 0.001–2% manganese in low and high alloy irons and steels.

EXPERIMENTAL AND DISCUSSION

The equipment used in the study consisted of a Hilger E492 spectrograph, an E.M.I. 9558-QB photomultiplier tube, a modulated argon-filled manganese hollow-cathode lamp[14] (Atomic Spectral, Melbourne), a tuned amplifier[14] and a 10-cm slot burner (Skinner, Melbourne). The width of the slot burner was increased from 0.040 to 0.075 cm during the study. With an air–acetylene flame, GATEHOUSE AND WILLIS[15] and ALLAN[11] respectively reported manganese sensitivities (1% absorption 2795 Å) of 0.05 and 0.06 p.p.m., and with an air–coal gas flame, GIDLEY[12] and HERRMANN AND LANG[16] respectively reported sensitivities of 0.07 and 0.10 p.p.m. With the present apparatus, the 2795 Å manganese line exhibited a maximum sensitivity of 0.05 p.p.m. and the respective sensitivities of the neighbouring 2798 Å and 2801 Å lines were 0.07 and 0.10 p.p.m.

The results of an investigation of the effect of different solvent acids and varying iron(III) concentrations on the absorption sensitivity of manganese are reported in Table I.

It can be observed that with the exception of nitric acid, the different acids cause a reduction in sensitivity and the addition of 10,000 p.p.m. of iron does not cause a further reduction in sensitivity. A 4.5% (v/v) phosphoric–4.5% (v/v) sulphuric acid mixture was selected as a suitable solvent and has the advantageous property of retaining tungsten and other acid-hydrolysable elements in solution; the manganese sensitivity under these conditions was 0.08 p.p.m. A 1-g sample of iron or steel dissolved in 30 ml of 15% (v/v) phosphoric–15% (v/v) sulphuric acid and diluted to 100 ml thus gives a working range of 0.000 to 0.100% manganese. Higher ranges of manganese can be analyzed by rotation of the burner to give a decreased absorption path length, and/or by the use of the less sensitive 2798 Å and 2801 Å lines. A smaller sample weight was not chosen because it was desired to use the same sample preparations for the simultaneous determination of chromium[17] and nickel[18] by atomic absorption spectrophotometry.

TABLE I

THE INFLUENCE OF SOLVENT ACIDS AND IRON CONCENTRATION ON THE ABSORPTION SENSITIVITY OF MANGANESE

(Lamp current, 8 mA; slot burner, 10 × 0.075 cm; entrance slit, 0.10 × 3 mm; flame, air (15 l/min S.T.P.)–acetylene (2.2 l/min S.T.P.); flame type, stoichiometric; absorption light path, 8 mm above base of flame)

Solvent medium	*Absorbance (2795 Å)*	
	10 p.p.m. Mn^{2+} *0 p.p.m. Fe^{3+}*	*10 p.p.m. Mn^{2+}* *10,000 p.p.m. Fe^{3+}*
Aqueous	0.640	—
10% (v/v) HNO_3	0.660	0.640
10% (v/v) HCl	0.585	0.585
10% (v/v) H_2SO_4	0.525	0.555
10% (v/v) H_3PO_4	0.525	0.525
4.5% (v/v) H_3PO_4–4.5% (v/v) H_2SO_4	0.535	0.540

The influence of the flame type and the height of absorption path in the flame were studied using test solutions which contained 0, 5 or 10 p.p.m. of manganese and 8,000 or 10,000 p.p.m. of iron(III) in 4.5% (v/v) phosphoric–4.5% (v/v) sulphuric acid. The maximum sensitivity (0.06 p.p.m.) was obtained with a slightly rich flame (hazy inner blue cone) and an absorption path 8 mm above the base of the flame; the sensitivity decreased to 0.08 p.p.m. in a rich or stoichiometric flame and decreased further in a lean flame. The stoichiometric flame was selected for further investigation because absorbance was independent of iron concentration in this flame; this is not the case with richer flames. With a constant set of experimental conditions, the manganese sensitivity was constant with hollow-cathode lamp currents between 6 and 16 mA. A helium-filled manganese hollow-cathode lamp became available in the later stages of the investigation but the sensitivity was not improved over that obtained with argon-filled lamps.

Interference study

An interference study was carried out on test solutions prepared according to the recommended procedure. The solutions contained 0.8 or 1 g of iron, the possible interfering elements being added as spectrographically pure metals. The manganese contents studied were 0.100%, 0.300% and 0.80% and interferences greater than 0.001%, 0.005% and 0.02% respectively were considered to be significant. Chromium at the 20% level caused positive interference in all flame types and in a stoichiometric flame the positive biases were equivalent to 0.005, 0.025 and 0.08% manganese respectively for the three manganese contents studied. It was evident that the optical absorption path would have to be confined to a smaller section of the flame and therefore the iris at the front of the hollow-cathode lamp and the entrance slit height were reduced progressively from 10 to 3 mm; the positive biases were then decreased to 0.001, 0.005 and 0.02% manganese respectively for the three manganese contents studied. The interference was eliminated finally by increasing the slot width of the burner from 0.040 to 0.075 cm. With slightly rich and rich flames, chromium still caused positive interferences although to a lesser extent than initially.

With the experimental conditions recorded in Table I, no significant interference was encountered from 30% Ni^{2+}, 30% Cr^{3+}, 10% W^{6+}, 10% Co^{2+}, 5% Mo^{6+}, 5% Cu^{2+}, 3% Si^{4+}, 2% V^{5+} or 0.5 % Al^{3+} either individually or in alloy combinations similar to the materials studied in Tables II and III. Calibration curves were prepared for the ranges 0–0.1%, 0–0.2%, 0–0.4%, 0–0.7%, 0–1.0% and 0–2.0% manganese and found to be linear.

The influence of entrance slit height and burner slot width as found in this study, indicated that as further improvements in hollow-cathode lamp technology take place, advantages will be derived from the use of pencil light beams which can be passed through small selected sections of laminar flames. The results obtained in these experiments indicated that manganese could be determined satisfactorily in low and high alloy irons and steels by atomic absorption spectrophotometry and this was confirmed in the subsequent investigations described below.

Reagents

Orthophosphoric (sp. gr. 1.75), sulphuric (sp. gr. 1.84), nitric (sp. gr. 1.42) and sulphurous (sp. gr. 1.03) acids. Manganese solution (1 ml ≡ 1 mg Mn): dissolve 1 g of manganese electrolytic chips (Baker Analyzed) in 20 ml of 25% (v/v) sulphuric acid, cool and dilute to 1 l. Johnson and Matthey iron sponge (manganese 3 p.p.m.).

Recommended procedure

Transfer 1 g of iron or steel to a 125-ml conical beaker. Prepare a calibration series by making suitable additions of manganese solution to several 1-g samples of iron sponge. Add 30 ml of 15% (v/v) phosphoric–15% (v/v) sulphuric acid, simmer to dissolve and oxidize with dropwise additions of nitric acid. The solution of certain classes of alloyed steels may be assisted by the use of aqua regia. Evaporate to fumes and fume gently for 1 min, extract the residue with 30 ml of water, add 5 drops of sulphurous acid and digest for 5 min to ensure solution of all soluble salts.

If necessary, filter through a Whatman 541 filter paper into a 100-ml graduated flask, rinse the beaker with several washes of hot 2% (v/v) sulphuric acid, wash the paper several times with hot 2% (v/v) sulphuric acid, allow to cool and dilute to the mark. Measure the absorbance using the experimental conditions set out in Table I and read the manganese content from the calibration graphs.

RESULTS

A series of low alloy irons and steels in the range 0–0.1% manganese were analyzed by the proposed procedure and the results reported to the nearest 0.001% are present-

TABLE II

MANGANESE CONTENT OF STANDARD IRONS AND STEELS IN THE RANGE 0–0.1% MANGANESE

Sample	*Composition*	*% Manganese*		
		Observed	*Certificate average*	*Certificate range*
J.M.-Grade 11[a]	Pure iron	0.004	0.001	—
B.C.S. 252	4% Ni, 0.5% V, 0.2% Cr – Steel	0.016 0.017(3) 0.018	0.016	0.012–0.023
N.B.S. 55d	Iron	0.028	0.030	0.028–0.031
N.B.S. 125a	3.3% Si – Steel	0.050	0.052	–[b]

[a] Johnson Matthey (London)
[b] Not finalised

TABLE III

MANGANESE CONTENT OF STANDARD IRONS AND STEELS IN THE RANGES 0.1%–0.2%, 0.2%–0.4%, 0.4%–0.7%, 0.7%–1.0%, 1.0%–2.0% MANGANESE

Sample	*Composition*	*% Manganese*		
		Observed	*Certificate average*	*Certificate range*
B.C.S. 251	5% Ni, 0.2% Mo–Steel	0.166 (2) 0.168 (3)	0.166	0.159–0.174
N.B.S. 153	8% Co, 8% Mo, 4% Cr, 2% W, 2% V – Steel	0.215	0.219	0.21 –0.227
N.B.S. 132a	6% W, 4% Mo, 4% Cr, 2% V – Steel	0.260 (2) 0.265 0.270 0.275	0.268	0.258–0.278
B.C.S. 253	3% Ni, 0.9% Mo, 0.5% Cu, 0.4% Cr, 0.2% V – Steel	0.360	0.355	0.346–0.360
N.B.S. 8h	Steel	0.45	0.454	0.448–0.461
B.C.S. 235	19% Cr, 9% Ni, 1% Cu, 0.7% W, 0.6% Ti – Steel	0.45	0.46	0 445–0.47
N.B.S. 10f	Steel	0.63 (3) 0.64 (2)	0.642	0.636–0.651
N.B.S. 101d	19% Cr, 9% Ni – Steel	0.74	0.739	0.734–0.746
N.B.S. 4i	1.4% Si, 0.2% Cu – Iron	0.78 (2) 0.80 (3)	0.793	0.779–0.804
N.B.S. 32e	1% Ni, 0.7% Cr, 0.1% Cu – Steel	0.80	0.798	0.792–0.806
N.B.S. 341	20% Ni, 2% Cr, 2% Si – Iron	0.92	0.92	0.90 –0.94
N.B.S. 100a	Steel	1.60 (2) 1.65 (3)	1.66	1.64 –1.68
N.B.S. 160a	19% Cr, 14% Ni, 3% Mo – Steel	1.65	1.62	1.61 –1.67

ed in Table II. The speed and ease of the procedure compares favourably with alternative established procedures for the range 0–0.100% manganese and the reproducibility and accuracy are excellent.

A series of low and high alloy irons and steels in the ranges 0.1%–0.2%, 0.2%–0.4%, 0.4%–0.7%, 0.7%–1.0% and 1.0%–2.0% manganese were analyzed by the proposed procedure and the results reported to the nearest 0.002%, 0.005%, 0.01%, 0.02% and 0.05% manganese respectively are presented in Table III. The results show excellent reproducibility and accuracy in the range 0.1 to 0.7% manganese and ready application to a wide range of iron and steel is indicated. Within the range 0.7 to 2.0% manganese, satisfactory application especially to highly alloyed iron and steel is indicated, although the accuracy obtainable is less than that of some established procedures.

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SUMMARY

A procedure is described for the determination of 0.001–2% of manganese in low and high alloy irons and steels by atomic absorption spectrophotometry. The sample is dissolved in phosphoric–sulphuric acid and atomised in an atomic absorption spectrophotometer. The method is rapid, free from interferences, preliminary separations are not required and results obtained on standard samples agree closely with stated certificate values.

RÉSUMÉ

Une méthode est décrite pour le dosage du manganèse (0.001–2%) dans le fer et l'acier, au moyen de la spectrophotométrie par absorption atomique. L'échantillon est dissous dans un mélange acide phosphorique–acide sulfurique et atomisé. Ce procédé est rapide, exempt d'interférences; des séparations préliminaires ne sont pas nécessaires.

ZUSAMMENFASSUNG

Es wird ein Verfahren zur Bestimmung von 0.001–2% Mangan in niedrig und hochlegierten Stählen mit der atomaren Absorptionsspektroskopie beschrieben. Die Probe wird in einem Gemisch aus Phosphor- und Schwefelsäure gelöst und im Absorptionsspektralphotometer zerstäubt. Die Methode erfordert keine vorhergehenden Trennungen. Sie ist schnell, frei von Störungen und führt zu guten Ergebnissen.

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AUTOMATIC ULTRAMICRO DETERMINATION OF IODINE IN NATURAL WATERS

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The classical iodimetric methods for the determination of iodine in water are time-consuming and require large samples[1]. More sensitive methods, based on the SANDELL–KOLTHOFF reaction[2] in which a trace of iodide or iodine accelerates the reduction of cerium(IV) by arsenious acid, have been developed. In one procedure[3] the absorbance of the cerium(IV) solution is measured after a fixed time and the iodide concentration of the sample is read from a suitable working curve. The inevitable technical difficulty and the errors associated with absorbance measurements taken while the reaction is in progress are greatly reduced by arresting the reaction at a given time by the addition of iron(II) and measuring the resulting red color of iron(III) thiocyanate developed after the addition of thiocyanate ions[4].

It was recently shown[5] that protein-bound iodine can be determined rapidly by an automatic reaction-rate method. Results are now presented which show that the same automatic procedure is well suited for the determination of iodine in water. The method is based on the catalytic effect of iodide on the reduction of cerium(IV) by arsenic(III). The time required for a small fixed (about 0.06 unit) change in absorbance is measured automatically and related directly to the iodide concentration.

The automatic procedure is simple, rapid, and requires much smaller quantities of sample than conventional methods. The sample is pipetted into the reaction cell containing cerium(IV) reagent, arsenic(III) is injected to start the reaction, the start button is pressed, and the data are read off a dial 1 to 2 min after the start for average samples. The measurements obtained on samples containing 1 to 15 μg of iodine/l are precise to within 0.2 μg of iodine/l. The relative error for the recovery of 25 and 50 μg of iodide added per litre of sample is within 3%.

EXPERIMENTAL

Equipment

The basic instrumental components are the same as those used previously[6,7] except for the following. Since the presently available spectro units (E. H. Sargent Co., Chicago 30, Ill.) use photoconductive cells of the same type as in the past (Hupp CDS - 10 cells) but less sensitive at 390 mμ, a 20 K Helipot was substituted for the 5K Helipot previously used[6]. The second modification was to reverse the position of the leads to the 1.5 V battery in the bridge circuit, because in the cerium(IV)–arsenic(III) reaction, the absorbance of the solution decreases as the reaction proceeds[5].

The temperature is controlled at 25° ± 0.1°. A narrow transmission band at 390 mμ is obtained by dialing the nominal 575 mμ second-order interference filter on the spectro unit and inserting a Corning No. 5970 filter in the auxiliary holder.

Reagents

All reagents are prepared in triple-distilled water. The iodide solutions are stored in glass-stoppered amber bottles and the cerium(IV) and arsenic(III) solutions in polyethylene bottles.

Sodium arsenite, 0.15 N. 7.5 g of As_2O_3 dissolved in 75 ml of 1 *N* sodium hydroxide and diluted to 1 l with water.

Ceric ammonium sulfate solutions. (*a*) *Solution I, 0.02 N.* 12.65 g of ceric ammonium sulfate, $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$, dissolved in 2.5 *N* sulfuric acid and diluted with the acid to 1 l. (*b*) *Solution II, 0.0024 N.* 12 ml of solution I mixed with 80 ml of 2.5 *N* sulfuric acid in a 100-ml volumetric flask. Then 5 ml of concentrated hydrochloric acid are added and the solution is diluted to the mark with 2.5 *N* sulfuric acid. This solution is prepared fresh every week and is allowed to age for 2 h before use.

Standard iodide solutions. (*a*) *Stock solution I.* 130.8 mg of potassium iodide dissolved in water and diluted to exactly 1 l in a volumetric flask; this solution contains 100,000 p.p.b. of iodide. (*b*) *Working solutions II.* Solutions containing 1000 and 10,000 p.p.b. of iodide are prepared from stock solution I by appropriate dilution. These solutions are used for the addition of known amounts of iodide to the water samples. (*c*) *Working standards III.* Standards containing 3, 6, 9, and 15 p.p.b. of iodide are prepared from the 1000 p.p.b. solution by appropriate dilution. They are used for the determination of the blank.

All working standards, reagent solutions and samples are kept in a water bath at 25° ± 0.1° when used.

Procedure

Preparation of equipment. Switch the Spectro–Electro titrator to the Spectro position about 2 h before the measurements are started to insure good stability from the light source. Dial the 575 position on the filter wheel and place the Corning No. 5970 filter in the auxiliary holder; throw the polarity switch to position 1. Before the measurements are started, turn the comparator unit to *on* and the range selector switch to *PNP*.

Preparation of water samples. (*a*) *Low-range procedure.* In the method of standard addition, measurements are taken for 3 solutions, solution A being the unknown water sample and solutions B and C containing in addition 10 and 5 p.p.b. of iodide respectively. To prepare solution B, transfer 0.250 ml of the 1000 p.p.b. of iodide solution to a 25-ml volumetric flask using a 0.25-ml syringe and dilute to the mark with solution A. To prepare solution C, mix 5 ml of solution A with 5 ml of solution B. (*b*) *High-range procedure.* Solution A is the unknown water sample and solutions B and C contain in addition 100 and 50 p.p.b. of iodide respectively. To prepare solution B, transfer 0.250 ml of the 10,000 p.p.b. of iodide solution to a 25-ml volumetric flask and dilute to the mark with solution A. To prepare solution C, mix 5 ml of solution A with 5 ml of solution B. For the determination of iodine only 3 ml each of solutions B and C are needed; however, larger quantities are prepared so as to permit sedimentation of suspended impurities and to have sufficient water for rinsing the pipets.

Measurement step. (*a*) *Low-range procedure* (Used for the range 0 to 50 p.p.b. of iodide). Set the comparator zero adjust at 5.90. Pipet 1.00 ml of cerium solution II and 3.00 ml of sample or standard iodide solution into the reaction cell, throw the comparator reagent selector switch to position 1 to start the stirring and adjust the Spectro balance control so that the meter needle is at the center. Set the comparator zero adjust at 4.50, and 1 min after the start of the stirring inject 0.250 ml of the arsenite solution into the cell using a 0.25-ml syringe and press the start button *at once* on the reaction rate adapter. The analysis is completed automatically and the number on the readout dial is recorded. Empty the cell by inserting an aspirator tube and rinse with water. Repeat the procedure for each analysis. (*b*) *High-range procedure* (Used for the range 50 to 250 p.p.b. of iodide). This procedure is similar to the low-range procedure except that the zero adjust is set first at 7.00, and then, after the needle has been adjusted to zero by the Spectro balance control, at 2.00.

Determination of blank. Standard solutions containing 3, 6, 9, and 15 p.p.b. of iodide are run as for the low-range procedure and reciprocal times are plotted linearly against the concentration of the standards. The straight line intercepting the abscissa gives the blank.

Calculations. The sample concentration in p.p.b. of iodide is read directly from a working curve obtained by plotting reciprocal of readout *vs.* iodide concentration. Solution A — the water sample without added iodide — is plotted as 0 p.p.b. of iodide and its actual concentration is obtained from the intercept of the working curve with the abscissa. The blank should be subtracted from this value.

RESULTS AND DISCUSSION

Table I shows the results as read directly from the readout dial of the automatic system for a typical series of determinations. Duplicate determinations were run to illustrate the reproducibility of the method. The data indicate that reproducibility for each sample is within 1 to 2% which is also typical of many similar series run over several months. The values for iodine in water samples obtained by the standard addition method are compared with those obtained by using a calibration curve, as shown in Table II. The differences between the values obtained by the 2 methods vary from 0 to 3.4 p.p.b. of iodide. Water samples from Urbana, Ill. (sample C) were analyzed over a period of a year and the results obtained by the standard addition method were always lower (by 2.5 to 3.8 p.p.b. of iodide) than those obtained by using a calibration curve.

The reciprocals of the average readout values from Table I are plotted against concentration in Fig. 1. If the rate of the reaction in all water samples was the same for the same iodide concentration, the working curves would have the same slope and the product of the iodide concentration in p.p.b. multiplied by the measurement time in sec, [I]*t*, would be the same for all samples. However, it can be seen from Fig. 1 and Table I that this is not the case. The difference in slope and the large variation in the value of the product [I]*t* (about 540 to 700) are due to interfering substances that affect the rate of the reaction. Any substance that oxidizes arsenic(III) or reduces cerium(IV) under the conditions of the procedure, constitutes a potential interference. In addition, large amounts of salts reduce the rate of the reaction

TABLE I

AUTOMATIC RESULTS FOR IODIDE

Sample	*Direct time readout (sec)*	*Iodide concn. · time*
3 p.p.b. iodide	126.7, 127.3	
6 p.p.b. iodide	76.0, 74.7	533–542
9 p.p.b. iodide	52.6, 52.9	
15 p.p.b. iodide	33.2, 32.7	
A[a]	269.7, 271.9	
A + 5 p.p.b. iodide	84.0, 85.4	595–610
A + 10 p.p.b. iodide	48.6, 48.9	
B[a]	68.8, 68.4	
B + 5 p.p.b. iodide	44.4, 45.9	620–630
B + 10 p.p.b. iodide	33.1, 32.5	
C[a]	49.9, 49.3	
C + 12 p.p.b. iodide	26.7, 26.4	698–710
C + 24 p.p.b. iodide	18.4, 18.2	

[a] Water samples A, B and C obtained from Chicago, Illinois, Denver, Colorado and Urbana, Illinois respectively.

TABLE II

COMPARISON OF STANDARD ADDITION METHOD AND CALIBRATION CURVE RESULTS FOR THE DETERMINATION OF IODINE IN WATER

Sample no.	*Iodine (p.p.b.)*	
	Standard addition method	*Calibration curve*
1	1.0	0.8
2	7.8	6.7
3	13.1	9.7
4	0.9	0.7
5	2.6	1.2
6	2.7	1.9
7	5.5	5.5
8	1.2	1.1
9	6.6	6.4

because of a decrease in activity of the components of the system[4]. To compensate for the effect of such interferences the composition of the standard iodide solutions should be similar to the samples. However, since interfering substances are present in different amounts in the various samples, it is not feasible to prepare such standard iodide solutions. It is therefore concluded that the use of a calibration curve obtained with pure solutions of potassium iodide in distilled water can often lead to erroneous results (Table II) and that the standard addition method described here should be applied. By applying the standard addition method it is assured that the concentration of all substances (except iodide) would be the same in all iodide solutions used in each analysis.

The straight line 1 obtained with standard iodide solutions does not pass through zero because of iodide present as contaminating agent in the reagents used. This contamination was equivalent to 1.2 p.p.b. of iodide. To establish the amount of iodine present in the various reagents the procedure described for the determination of the blank was carried out with various amounts of any one reagent, HCl or H_2SO_4 or As(III) or Ce(IV), that is ordinarily used, and from the result the content of iodine in the added reagent was calculated. Sulfuric acid and ceric ammonium sulfate were found to be iodine-free. Hydrochloric acid and sodium arsenite were the sources of contamination; the sum of their iodine content corresponded to the established blank of 1.2 p.p.b. of iodide and it was therefore concluded that the triple-distilled water used was iodine-free. A blank is determined whenever new solutions or reagents prepared from new lots of reagents are to be made.

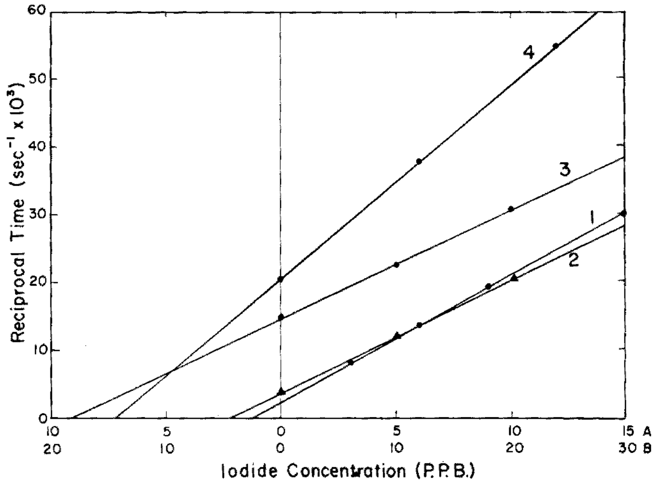

Fig. 1. Plot of reciprocal time *vs.* iodide concentration. (1) Determination of blank; (2, 3, 4) potable water samples.

The determination of iodine in water is an exceedingly delicate analysis, and scrupulous care should be exercised to prevent contamination of the samples with extraneous iodine. Glassware used for the iodine determination should be reserved for this purpose exclusively.

The method has been applied for a large number of natural (mainly potable) waters. A few typical results are shown in Table III. The same results were obtained

TABLE III

DETERMINATION OF IODINE IN NATURAL WATERS

Sample no.	*Origin*	*Iodine (p.p.b.)*
1	Urbana, Illinois	13.1, 12.8
2	Chicago, Illinois	1.0
3	Milwaukee, Wisconsin	1.2
4	Denver, Colorado	7.8
5	Rantoul, Illinois	6.6
6	Ashkum, Illinois	23.8, 23.1
7	Sarnia, Canada	0.9
8	Flossmoor, Illinois	5.5

whether the iodine added was in the form of iodide or iodate. Sample 6 was analyzed by the low-range procedure and it was found to contain 23.8 p.p.b. of iodine. Since the measurement times for solutions A, B, and C were very close to each other, this sample was also analyzed by a slightly modified procedure — addition of 10 and 30 p.p.b. of iodide and comparator zero adjust set at 4.00 — and was found to contain 23.1 p.p.b. of iodine. The agreement between the two results is typical of many similar analyses.

Most of the natural waters contain 0 to 15 p.p.b. of iodine and the low-range procedure should be followed. However, if the measurement time by the low-range procedure is less than 20 sec, the high-range procedure should be followed. No work was done with sea waters, but the method could also be used for the analysis of such samples.

TABLE IV

RECOVERY OF IODIDE ADDED TO SAMPLES OF WATER

Sample no.	*Iodide concentration (µg/l)*				*Recovery (%)*
	Originally present[a]	*Added*	*Total*	*Found*[a]	
1	12.6	50	62.6	61.0	97
2	7.8	25	32.8	32.1	97
2	7.8	50	57.8	57.7	100
3	1.4	25	26.4	26.9	102
3	1.4	50	51.4	51.4	100
4	6.6	50	56.6	56.3	99
				Average	99.2

[a] Average of two determinations.

Because standard reference samples were not available, an indication of the accuracy of the method was determined by analyzing several samples to which known amounts of iodide had been added. The iodide concentrations of 4 different samples of water were determined according to the low-range procedure by averaging the results of duplicate analyses made on each of the samples. Then known amounts of iodide, 25 and 50 µg/l, were added to each, and the final iodide concentrations were determined by averaging the results obtained by analysis of each sample in duplicate. The recovery of iodide varied from 97 to 102% with an average value of 99.2 (Table IV).

This research was supported in part by the National Institutes of Health, Public Health Service, Research Grant GM 11039-01.

SUMMARY

An automatic spectrophotometric reaction rate method is described for the ultramicro determination of iodine in natural waters. The method is based on the catalytic effect of iodine on the reduction of cerium(IV) by arsenic(III). The time required for a small fixed (about 0.06 unit) change in absorbance is measured automatically and related to the iodine concentration. Speed and the small size of the sample needed are the main advantages over other methods. Iodine in water in the range 1 to 15 µg/l in a total volume of 4 ml is determined with errors smaller than ± 0.3 µg/l.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour l'ultramicrodosage automatique de l'iode dans les eaux naturelles. Elle est basée sur l'effet catalytique de l'iode sur la réduction du cérium(IV) par l'arsenic(III). Le temps nécessaire pour obtenir une variation déterminée de l'absorption (environ 0.06 unités) est mesuré automatiquement. Principaux avantages: rapidité et grande sensibilité. On peut doser ainsi des teneurs en iode de 1 à 15 µg/l, dans un volume de 4 ml, avec une erreur inférieure à 0.3 µg/l.

ZUSAMMENFASSUNG

Es wird eine automatische spektralphotometrische Methode zur Ultramikrobestimmung von Jod in natürlichen Wässern beschrieben. Die Methode beruht auf einem katalytischen Effekt des Jods auf die Reduktion von Cer(IV) durch Arsen(III). Die Zeit, die für einen Wechsel in der Extinktion benötigt wird, wird automatisch gemessen und dient als Mass für die Jodkonzentration. Schnelligkeit und geringe Probengrösse sind die Hauptvorteile gegenüber anderen Methoden. In einem Volumen von 4 ml lässt sich das Jod im Bereich von 1–15 µg/l mit einem Fehler von weniger als ± 0.3 µg/l bestimmen.

REFERENCES

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[3] J. R. ROSSUM AND P. A. VILLARRUZ, *Jour. AWWA*, 52 (1960) 919.
[4] M. DUBRAVCIC, *Analyst*, 80 (1955) 295.
[5] H. V. MALMSTADT AND T. P. HADJIIOANNOU, *Anal. Chem.*, 35 (1963) 2157.
[6] H. V. MALMSTADT AND S. I. HADJIIOANNOU, *Anal. Chem.*, 34 (1962) 452.
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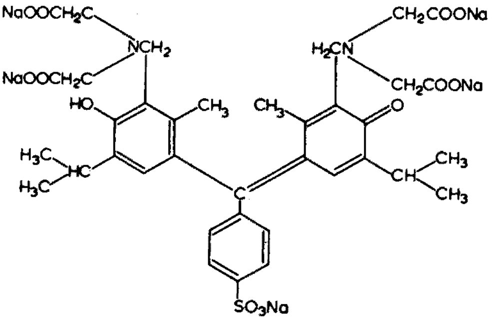
Short Communication

3′, 3″-Bis {[N, N-bis (carboxymethyl) amino] methyl}-thymolsulfonephthalein (pentasodium salt) as a chromogenic reagent

A large number of triphenylmethane dyes are known to produce colored complexes with various metallic ions in solution. The complexes formed have usually a high value of stability and have often been utilized in the absorptiometric as well as complexometric determination of various metal ions at a microlevel.

The present communication reports in detail the color-forming reactions of 3′,3″-bis{[N,N-bis(carboxymethyl)amino]methyl}-thymolsulfonephthalein (pentasodium salt; thymolsulfonephthalexon; TSP) with a variety of metal ions. The reagent is represented by the structure:



Přibil *et al.*[1,2] have used a similar reagent for the determination of manganese(II) and other ions.

A 0.001 *M* solution of thymolsulfonephthalexon (reagent grade; Eastman Organic Chemicals) was prepared in double-distilled water. Solutions of the metal ions were prepared from analytical-grade reagents to give a final concentration of 1 mg/ml. A sodium acetate–acetic acid buffer was prepared by mixing proper amounts of 2 *N* solutions of both sodium acetate and acetic acid.

Two drops of the buffer were added to one drop of the metal ion solution and finally to one drop of the reagent. The mixture was diluted to 2 ml with water and the color observed. Colors are mostly stable in a neutral or mildly acidic medium.

The reagent itself undergoes changes in color depending upon the hydrogen-ion concentration of the medium. The various absorption maxima shown by the reagent at different pH values are represented graphically in Fig. 1.

Color reactions with metal ions and the conditions employed are listed in Table I.

Studies on the characteristics of the complexes formed are in progress. The composition, stability and the possible analytical applications of the chelates of the reagent with various metal ions including the lanthanons are being investigated by absorptiometric as well as polarographic measurements. The molecule has in addition to the

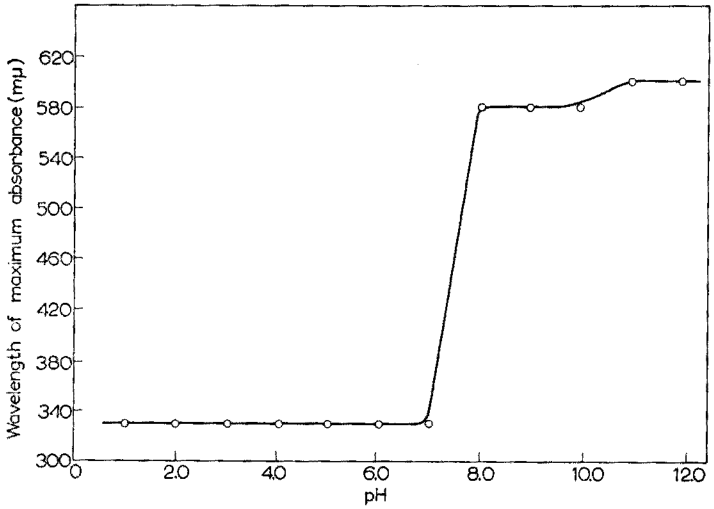


Fig. 1. Effect of pH on the absorbance maxima of TSP (concn. $5 \cdot 10^{-5}$ *M*)

TABLE I

COLOR REACTIONS OF TSP WITH INORGANIC IONS

Metal ion	*Used as*	*Color observed (at pH 6; unless otherwise stated)*	*Remarks*
Cu(II)	$Cu(NO_3)_2 \cdot 6H_2O$	Blue	—
Ag(I)	$AgNO_3$	Slight pink to brown	Probably due to reduction
Mg(II)	$MgCl_2 \cdot 6H_2O$	Slight greenish tinge	—
Be(II)	$Be(NO_3)_2 \cdot 3H_2O$	Pink	—
Zn(II)	$Zn(NO_3)_2 \cdot 6H_2O$	Blue	—
Cd(II)	$Cd(NO_3)_2 \cdot 4H_2O$	Blue	—
Al(III)	$Al(NO_3)_3 \cdot 9H_2O$	Pink	—
Ga(III)	$GaCl_3$	Blue	—
Ce(III)	$Ce(NO_3)_3 \cdot 6H_2O$	Blue	—
Ti(IV)	$TiCl_4$	Pink	—
Zr(IV)	$ZrOCl_2 \cdot 8H_2O$	Blue at pH 2–5	Purple in neutral to mildly acidic media
Hf(IV)	$HfOCl_2 \cdot 8H_2O$	Blue at pH 2–5	Purple in mildly acidic or neutral media
Pb	$Pb(NO_3)_2$	Blue	—
Th(IV)	$Th(NO_3)_4 \cdot 4H_2O$	Blue	Stable in fairly acidic media
VO	$VOSO_4$	Blue	Pink in highly acidic media, tends to fade
VO_3^-	$NaVO_3$	Blue	Green in mildly acidic media, in high concn. of acid fades to yellow but the greenish color reappears

TABLE I (Continued)

Metal ion	*Used as*	*Color observed (at pH 6; unless otherwise stated)*	*Remarks*
As(III)	As_2O_3	—	Pinkish in acidic media
Sb(III)	$SbCl_3$	—	Pinkish in highly acidic media
Sb(V)	Sb_2O_5	—	Pinkish in highly acidic media
Bi(III)	$Bi(NO_3)_3 \cdot 5H_2O$	Blue	Disappears in high acid concentrations
UO_2(II)	$UO_2(NO_3)_2 \cdot 6H_2O$	Pinkish above pH 5	Fades to yellow in acidic solutions; at pH 4, dirty brown
Mn(II)	$MnCl_2 \cdot 4H_2O$	Blue	Fades on increasing acidity
Fe(II)	$FeSO_4 \cdot 7H_2O$	Green	Consistent in mildly acidic media
Fe(III)	$Fe(NO_3)_3 \cdot 9H_2O$	Green	Consistent in mildly acidic media
Co(II)	$Co(NO_3)_2 \cdot 6H_2O$	Blue	—
Ni(II)	$Ni(NO_3)_2 \cdot 6H_2O$	Blue	—
Pd(II)	$PdCl_2$	Purple	—
Rare earths (III)	Chlorides	Blue	—
SO_3^{2-}	$NaHSO_3$	—	Slightly pink in acidic media

chromogenic phthalein group, two iminodiacetate groups, which account for the strong chelating properties of the reagent. The 2 nitrogen donors and the 4 acetate groups in the molecule may greatly influence the order of stability of the metal chelates.

Use of the reagent as a chelatochromic indicator in various metal–EDTA titrations has also shown significant promise. A method has been worked out for the compleximetric determination of thorium in the presence of rare earths and will be communicated later.

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SURESH C. SRIVASTAVA
ANIL K. MUKHERJI

1 R. PŘIBIL AND M. KOPANICA, *Chemist-Analyst*, 48 (1959) 35.
2 J. KÖRBL AND R. PŘIBIL, *Chem. Listy*, 51 (1957) 1804.

(Received November 1st, 1963)

Book Reviews

GEORG ALEXITS UND STEFAN FENYÖ, *Mathematik für Chemiker*, nach der 3. ungarischen Ausgabe in's Deutsche übersetzt von STEFAN FENYÖ, Gemeinschaftsausgabe des Akadémiai Kiadó, Budapest und der Akademischen Verlagsgesellschaft Geest und Portig K.-G., Leipzig, 1962, viii + 449 S., 238 Abbildungen, Preis $10.80.

Das Buch bringt stofflich etwa das, was der Chemiker während seines Studiums im allgemeinen an Mathematik benötigt. Nur wenige mathematische Grundkenntnisse werden vorausgesetzt. Das Buch beginnt mit dem Zahlenbegriff, dem Rechnen mit Ungleichungen, dem Funktionsbegriff, Koordinatensystemen, der Geraden und den trigonometrischen Funktionen, dann werden Grenzwert und Differentialquotient, Mittelwertssatz, das Rechnen mit Differentialen und die Taylor'sche Reihe behandelt. Nach Kapiteln über Integralrechnung, gewöhnliche Differentialgleichungen und Funktionen mit mehreren Variablen folgen schliesslich Einführungen in die Anwendung von Nomogrammen, in die Grundlagen der Wahrscheinlichkeitsrechnung sowie in die Behandlung partieller Differentialgleichungen und von Fourier-Reihen.

Die Darstellung des Stoffes ist klar, leicht verständlich und didaktisch geschickt. Beispiele für die Anwendung des Besprochenen auf chemische Probleme sind in grösserer Zahl eingestreut, was der meist in erster Linie auf das Stoffliche gerichteten Denkweise des Chemikers entgegenkommt. An die einzelnen Kapitel sind insgesamt mehr als 250 Übungsaufgaben angeschlossen, deren Lösungen am Schlusse des Buches gegeben werden. Für ein Selbststudium ist das Buch offensichtlich gut geeignet, allerdings wird der Chemiker, welcher sich später den stärker mathematisch orientierten Spezialgebieten der physikalischen Chemie, der Strukturanalyse, der Verfahrenstechnik, der Valenztheorie usw. widmet, mit dem hier gebrachten nicht auskommen. So sind die Vektorrechnung und die Fourieranalyse nur kurz behandelt und auf das Rechnen mit Matrizen ist nicht eingegangen worden.

Die Übersetzung in die deutsche Sprache ist ausgezeichnet gelungen. Druck und Ausstattung sind gut.

H. BODE (Hannover)

Anal. Chim. Acta, 30 (1964) 498

R. M. SILVERSTEIN AND G. C. BASSLER, *Spectrometric Identification of Organic Compounds*, John Wiley and Sons, London-New York, 1963, 177 pp., price £3.4/—.

The ease with which many elegant instrumental and especially spectroscopic measurements can be made, has led to their ever increasing use for routine analytical purposes. This book, derived from a series of lectures, attempts to supply the background and experience necessary for the successful use of these techniques. The first part of the book deals briefly with the correlations between structure and spectral properties that have been established for nuclear magnetic resonance, ultraviolet, infrared, and mass spectra. In the available space (100 pages) only cursory accounts can be given which, through their superficiality, are unfortunately misleading in their apparent support of the fallacy that the structural assignments are both simple and automatic. The second part of the book is devoted to 40 problems in which a structure is to be deduced from

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the spectral data. Solutions to half of the problems are worked, albeit in many cases with a surprising facility. Nevertheless the complete set of problems provides a useful if expensive collection. The book is handsomely produced and printed.

K. J. MORGAN (Birmingham)

Anal. Chim. Acta, 30 (1964) 498–499

Absorption Spectra in the Ultraviolet and Visible Region, Edited by L. LÁNG, Publishing House of the Hungarian Academy of Sciences, Budapest, Vol. III, 1962, 424 pp., price $ 16.00; Vol. IV, 1963, 414 pp., price $ 16.00.

Les volumes III et IV de la collection *Absorption Spectra in the Ultraviolet and Visible Region* édité par le Dr. L. LÁNG ont été publiés respectivement en 1962 et 1963. Ces nouveaux ouvrages sont présentés sous la même forme que les volumes précédents mais alors que les premiers étaient uniquement originaires de laboratoires hongrois et polonais, les nouveaux proviennent également d'une collaboration d'auteurs anglais, russes et tchèques.

Le volume III de 424 pages et le volume IV de 414 pages contiennent ensemble les données spectrophotométriques (spectres, tableau des extinctions à différentes longueurs, conditions opératoires — solvant, épaisseur cellule, température) d'environ 350 substances organiques.

Chaque ouvrage comporte également à la fin un index des formules et un index des matières.

Il s'agit donc là d'une information particulièrement précieuse pour les chimistes qui se trouvent confrontés avec des problèmes d'analyses et d'identification.

G. DUYCKAERTS (Liége)

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Announcements

1965 INTERNATIONAL CONFERENCE

MODERN TRENDS IN ACTIVATION ANALYSIS

An International Conference on Activation Analysis will be held at Texas A & M University, College Station, Texas, U.S.A., during April, 1965. Cooperating sponsors are the International Atomic Energy Agency, the Division of Isotopes Development (United States Atomic Energy Commission) and the Activation Analysis Research Laboratory of Texas A & M University.

Further information can be obtained from:

Dr. Derek Gibbons, Wantage Research Laboratory, U. K. Atomic Energy Authority, Wantage, Berkshire, England, or

Dr. Richard E. Wainerdi, Activation Analysis Research Laboratory, Texas A & M University, College Station, Texas, U.S.A.

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1964 GORDON RESEARCH CONFERENCES IN NEW HAMPSHIRE

FIFTY INTERNATIONAL CONFERENCES SCHEDULED ON MOST ACTIVE AREAS OF BASIC RESEARCH

The Gordon Research Conferences, international Conferences on Developments in the most active areas of basic research, will include fifty, full-week sessions this summer. The program includes nine new research topics.

Scheduled to open on 15 June, the Conferences will continue through 4 September. The meetings, each devoted exclusively to a single subject and lasting a week, will be held at five locations in New Hampshire: NEW LONDON (Colby Junior College), NEW HAMPTON (New Hampton School), MERIDEN (Kimball Union Academy), TILTON (Tilton School) and ANDOVER (Proctor Academy).

Founded 33 years ago, and originally only two in number, the Conferences are designed to promote the creative interchange of ideas and communications among research leaders in various scientific disciplines and in different scientific environments — academic, government and industrial.

The 1964 Conference subjects are:

NEW LONDON, *Hydrocarbon Chemistry* (June 15–19); *Nuclear Chemistry* (June 22–26); *Catalysis* (June 29–July 3); *Polymers* (July 6–10), *Textiles* (July 13–17); *Elastomers* (July 20–24); *Corrosion* (July 27–31); *Medicinal Chemistry* (Aug. 3–7); *Food and Nutrition* (Aug. 10–14); *Separation and Purification* (Aug. 17–21); *Cancer* (Aug. 24–28); *Nuclear Structure Physics* (Aug. 31–Sept. 4).

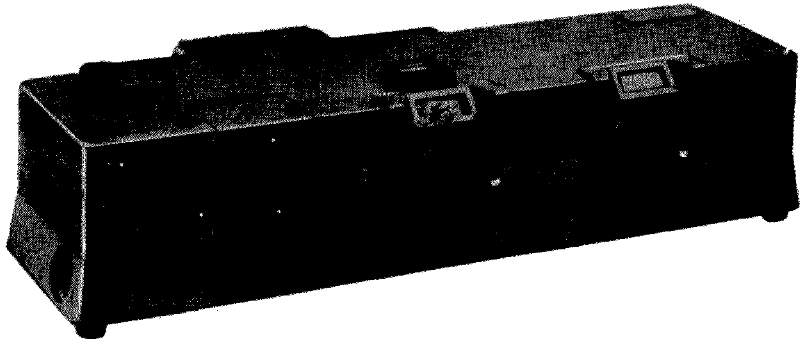
NEW HAMPTON, *Environmental Sciences,* Microchemical Contaminants in Water (June 15–19); *Nucleic Acids* (June 22–26); *Theoretical Chemistry* (June 29–July 3); *Metals and Metal Binding in Biology* (July 6–10); *Statistics in Chemistry and Chemical Engineering* (July 13–17); *Scientific Information Problems in Research,* Critical Tables (July 20–24); *Radiation Chemistry* (July 27–31); *Steroids and Other Natural Products* (Aug. 3–7); *Inorganic Chemistry* (Aug. 10–14); *Analytical Chemistry* (Aug. 17–21); *Chemistry of Heterocyclic Compounds* (Aug. 24–28); *Adhesion* (Aug. 31–Sept. 4).

MERIDEN, *Lipid Metabolism* (June 15–19); *Solid State Studies in Ceramics* (June 22–26); *Cell Structure and Metabolism* (June 29–July 3); *Coenzymes and Metabolic Pathways* (July 6–10); *Chemistry, Physiology and Structure of Bones and Teeth* (July 13–17); *Physical Metallurgy* (July 20–24); *Chemistry at Interfaces* (July 27–31); *Toxicology and Safety Evaluations* (Aug. 3–7); *Dissolution and Crystallization of Calcium Phosphates* (Aug. 10–14); *Chemistry and Physics of Solids* (Aug. 17–21); *Infrared Spectroscopy* (Aug. 24–28); *Nonlinear Optics* (Aug. 31–Sept. 4).

TILTON, *Biochemistry and Agriculture* (June 15–19); *Friction, Lubrication, and Wear* (June 22–26); *Chemistry and Physics of Space* (June 29–July 3); *Chemistry of Carbohydrates* (July 6–10); *Chemistry and Physics of Isotopes* (July 13–17); *Organic Reactions and Processes* (July 20–24); *High-Temperature Chemistry* (July 27–31); *Biopolymer-Solvent Interactions and the Structure of Liquids* (Aug. 3–7); *Organic Photochemistry* (Aug. 10–14); *Geochemistry,* Water (Aug. 17–21); *Chemistry and Metallurgy of Semiconductors* (Aug. 24–28); *Ionic Movements and Interactions in Biological, Chemical, and Physical Phenomena* (Aug. 31–Sept. 4).

ANDOVER, *Biomathematics* (July 13–17); *Biological Regulatory Mechanisms* (July 20–24).

Further information, including a complete schedule of Conferences and attendance application forms, may be obtained from Dr. W. George Parks, Director, Gordon Research Conferences, University of Rhode Island, Kingston, Rhode Island.



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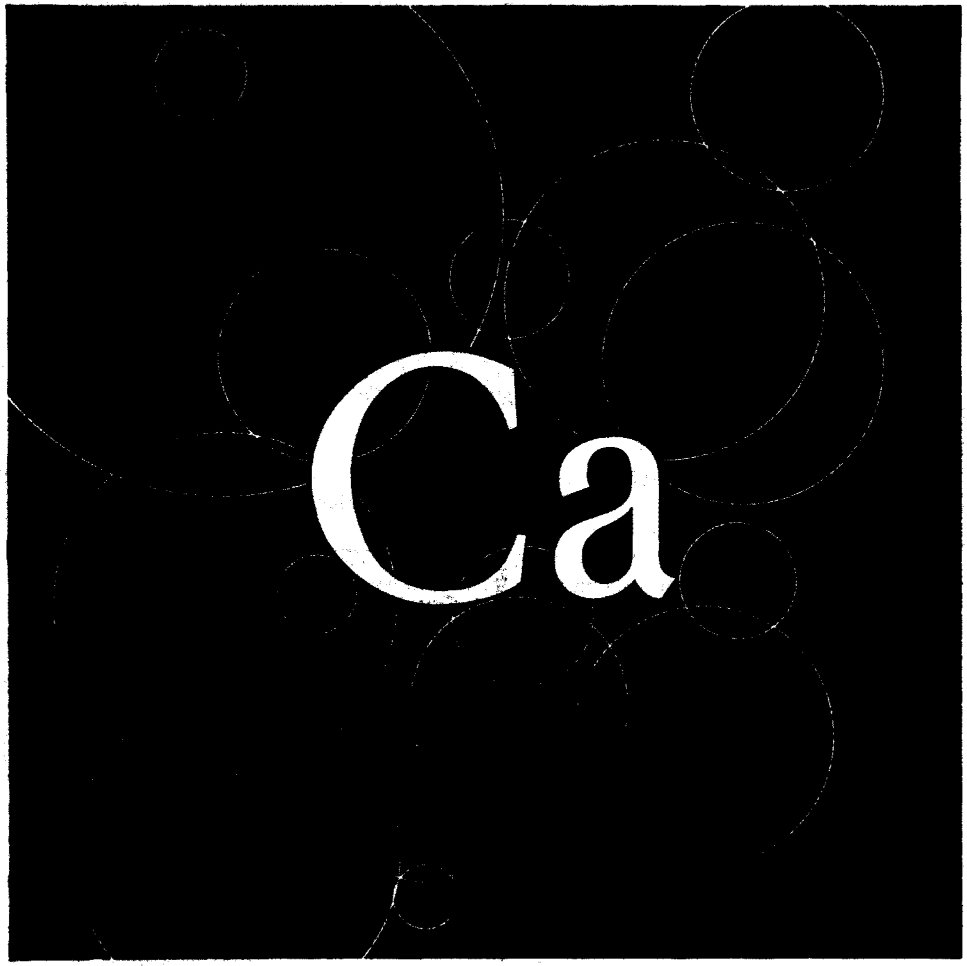
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