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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 24, No. 5, May 1961

THE CHARACTERISATION AND DETERMINATION OF NITROGENOUS ORGANIC BASES IN MIXTURES WITH AMMONIUM REINECKATE

The reaction between nitrogenous organic bases and ammonium reineckate was studied and was found to depend on the basicity of the bases and the pH of the reaction media. An expression is given which relates the dissociation constant pK_b of a base and the pH of the reaction; when the pK_b of a base is known the pH required for the complex formation can be calculated. The conditions for the formation of reineckates of very weak bases together with the formation of mono- and di-reineckates of dibasic substances are given. The separation of bases whose pK_b values are sufficiently far apart and the determination of mixtures of mono- and dibasic substances were effected by pH adjustment of the reaction media. The isolation of strychnine from putrified human livers is also described.

L. Kum-Tatt, *Anal. Chim. Acta*, 24 (1961) 397–409

OPTIMUM "COOLING TIME" TO MINIMIZE INTERFERING ACTIVITY IN NON-DESTRUCTIVE ACTIVATION ANALYSIS

In order to choose the best "cooling time" to minimize interfering γ-rays in activation analysis, the "cooling time" has been examined theoretically. There is an optimum cooling time which depends on the time of irradiation and on the half-life of nuclide formed to be determined.

M. Okada, *Anal. Chim. Acta*, 24 (1961) 410–412

THE COMPOSITION OF RHODAMINE B CHLOROGALLATE

The formula of rhodamine B chlorogallate has been shown to be $(RH)GaCl_4$ where R = rhodamine B.

F. Culkin and J. P. Riley, *Anal. Chim. Acta*, 24 (1961) 413–414

VOLUMETRIC DETERMINATION OF PERSULPHATE IN SULPHURIC SOLUTIONS BY PERMANGANATE

The determination of persulphate in a *ca.* 12.5 N sulphuric acid solution by direct titration with permanganate is described. The results are satisfactory but the conditions are critical.

Y. K. Gupta, *Anal. Chim. Acta*, 24 (1961) 415–418

IODIMETRIC DETERMINATION OF CARBON DISULPHIDE

STUDY OF THE EFFECT OF pH

The effects of pH and time on the error (due to decomposition of xanthate) involved in the iodimetric determination of carbon disulphide have been studied. A pH range of 5.4 to 5.8 (acetate-buffered) is recommended. Carbon disulphide varying in amount from 0.0060 to 0.3240 g can be determined with an error of ±1.0%.

M. Eusuf and M. H. Khundkar, *Anal. Chim. Acta*, 24 (1961) 419–423

COMPLEXOMETRIC DETERMINATION OF CHLORIDES, CHLORATES AND PERCHLORATES IN PRESENCE OF EACH OTHER

(in French)

A method is described for the analysis of a mixture of chlorides, chlorates and perchlorates by complexometric titration. It is based on the partial reduction of chlorates and the reduction of chlorates plus perchlorates respectively; the chloride formed can then be determined.

A. DE SOUSA, *Anal. Chim. Acta*, 24 (1961) 424–426

THERMOGRAVIMETRIC CHARACTERISTICS OF BARBITURIC ACID AND SOME OF ITS DERIVATIVES

The thermolysis curves of barbituric acid and some of its derivatives have been determined. Barbituric acid, violuric acid and dilituric acid form hydrates while 1,3-dimethylvioluric acid and barbital are anhydrous. Barbital and 1,3-dimethylvioluric acid sublime before decomposition. The differential thermal analysis for dilituric acid showed a sharp exotherm at 190° indicating a violent explosion.

A. BERLIN, M. E. TAYLOR AND R. J. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 427–431

THERMOGRAVIMETRIC AND MAGNETIC CHARACTERISTICS OF SOME INORGANIC SALTS OF DILITURIC ACID

The thermolysis curves of the transition metal diliturates as well as those of copper, zinc, cadmium, ammonium and rubidium have been determined. These diliturates with the exception of ammonium and rubidium diliturates form hydrates. The oxides of the corresponding metals are obtained at relatively low temperatures. Magnetic susceptibility measurements show that these compounds are "essentially ionic" salts.

A. BERLIN AND R. J. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 432–437

OBSERVATIONS ON THE USE OF AN ANION EXCHANGE RESIN IN THE DETERMINATION OF AMINOBENZOIC ACIDS, AMINOPHENOLS AND SOME RELATED SUBSTANCES IN BIOLOGICAL MATERIALS

An anion exchange resin (Dowex 1X10) has been studied for the purpose of separating aminobenzoic acids, aminophenols, sulphanilamide and nicotinic acid, preparatory to their determination by colorimetric methods.

S. L. TOMPSETT, *Anal. Chim. Acta*, 24 (1961) 438–443

CHROMATOGRAPHIC SEPARATION OF IONS IN PRESENCE OF OXALATE, TARTRATE AND CITRATE, WITH AQUEOUS ETHANOL AS SOLVENT. I

The paper chromatographic separation of Ag, Hg, Pb, Bi, Cu, Cd, Co, As(III), Sb(III) and Sn(II) in mixtures of 3, 4 or 5 of these ions has been studied in the absence and presence of oxalate, citrate and tartrate with aqueous ethanol as solvent.

E. J. SINGH AND A. K. DEY, *Anal. Chim. Acta*, 24 (1961) 444–445

QUANTITATIVE CHROMATOGRAPHIC ANALYSIS USING RECTIFIED RADIO-FREQUENCY METHODS. I. LITHIUM, SODIUM AND POTASSIUM

The BLAKE Zone Detector has been shown to be a very useful apparatus for the location of ion zones separated by paper chromatography. In the case of the alkali metals, these zones can be estimated by measuring the impedance of their aqueous extract. An alternative method, that of measuring the area under the detector curve, does not provide a practical means of quantitative measurement. A new developing solvent is described for the paper chromatographic separation of lithium, sodium and potassium chlorides.

J. A. BROOMHEAD AND N. A. GIBSON, *Anal. Chim. Acta*, 24 (1961) 446–450

DETERMINATION OF LEAD IN GASOLINE BY ATOMIC ABSORPTION SPECTROSCOPY

A procedure has been developed for the direct determination of lead in gasoline by atomic absorption spectroscopy. This procedure is rapid, does not require expensive equipment, is remarkably free from interference by other trace elements present, and allows considerable variation in the sulfur and nitrogen content of the gasoline. It compares favorably with other existing procedures for this determination, such as X-ray fluorescence, wet chemical methods, and flame photometry.

J. W. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 451–455

THE DETERMINATION OF INDIUM AND THALLIUM IN SILICATE ROCKS BY A COMBINED SOLVENT EXTRACTION AND SPECTROCHEMICAL TECHNIQUE

A technique has been developed for the determination of In and Tl at very low concentrations in silicate rocks. The iodo-complexes of these elements are extracted from the rock silicate into ethyl ether and the ethereal residues are analysed spectrochemically. The optimum working conditions were established by a study of the variation of percentage extraction as a function of hydrogen iodide normality; the reproducibility of the spectrochemical procedure was investigated. In and Tl were determined in eight silicate rocks including standard granite G-1 and standard diabase W-1. Good agreement was obtained with results of other workers for these two rocks and with the author's previous results. The evidence for a In/Mn coherence in silicate rocks is sufficiently strong to warrant further investigations.

R. R. BROOKS, *Anal. Chim. Acta*, 24 (1961) 456–462

CONTRIBUTIONS TO THE STUDY OF ORGANIC OSMIUM REAGENTS

The reaction of osmium is examined with two thiourea derivatives and four heterocyclic nitrogen compounds containing the SH-group attached to the ring, and five new colorimetric methods for the determination of osmium in the range 1.04–41.44 μg Os/ml are proposed.

GH. BAIULESCU, C. LAZĂR AND C. CRISTESCU, *Anal. Chim. Acta*, 24 (1961) 463–466

THIONIN DERIVATIVES IN THE EXTRACTION AND DIRECT PHOTOMETRIC DETERMINATION OF BORON

Thionin and nine commercially available thionin derivatives were studied for their applicability in the analytical solvent extraction and direct photometric determination of boron. Azure A, Azure B, Azure C, Methylene Blue, New Methylene Blue N, Methylene Green, Toluidine Blue O, Thionin and the eosinates of Azure A and B were investigated. Over thirty organic solvents, mostly chlorinated or brominated were tried with these dyes. 1,2-Dichloroethane, 1,2-dichloropropane, dichloromethane, 1,1,2-triochloroethane, *cis*-dichloroethylene, *o*-dichlorobenzene, 1,4-dichlorobutane and mixtures of these solvents proved applicable. Many good dye–solvent combinations were found which were very attractive for the separation and determination of various amounts of boron. Only thionin itself proved unsatisfactory.

L. PÁSZTOR AND J. D. BODE, *Anal. Chim. Acta*, 24 (1961) 467–473

DETERMINATION OF SULPHANILAMIDES WITH ALKYL NITRITES BY A POTENTIOMETRIC METHOD

A potentiometric titration with alkyl nitrite solutions is described for the determination of various sulpha drugs.

N. K. MATHUR, S. P. RAO AND O. P. KACHHAWAHA, *Anal. Chim. Acta*, 24 (1961) 474–475

OSCILLOPOLAROGRAPHIC DETECTION AND DETERMINATION OF IODATE AND PERIODATE

(in German)

The oscillopolarographic behaviour of periodate and iodate has been investigated in acid, neutral and alkaline electrolytes. The detection and determination of periodate in iodate may be carried out using iodate as electrolyte and the detection and determination of iodate in periodate may be carried out using 5 *M* sodium hydroxide as electrolyte.

A. BERKA AND J. DOLEŽAL, *Anal. Chim. Acta*, 24 (1961) 476–480

THE USE OF MICROCHEMICAL METHODS IN RADIOCHEMICAL ANALYSIS

Techniques used at A.W.R.E. during the past 6 years for the radiochemical analysis of mixtures of active nuclides using 0.5- to 1-mg quantities of carrier are described and their advantages discussed. Micro-methods are listed for chemical yield determinations by spectrophotometry and micro-titration, and details are given for the micro-titration of a number of elements with EDTA using a spectrophotometric end-point. A special fitment is described to enable the Unicam SP 600 spectrophotometer to be used for micro-titrations. Some values are given for the coefficients of variation obtained in typical chemical yield methods and in overall radiochemical determinations of ^{99}Mo, ^{111}Ag, ^{115}Cd and ^{140}Ba.

R. G. MONK AND J. HERRINGTON, *Anal. Chim. Acta*, 24 (1961) 481–492

DETERMINATION OF TUNGSTEN IN PRESENCE OF VANADIUM

(Short Communication; in French)

A. CLAEYS, *Anal. Chim. Acta*, 24 (1961) 493

SPOT TEST FOR BENZYLAMINE AND *p*-NITROBENZALDEHYDE

(Short Communication)

F. FEIGL AND V. ANGER, *Anal. Chim. Acta*, 24 (1961) 494–495

OBSERVATIONS ON THE THERMAL DECOMPOSITION OF CUPRIC ACETATE MONOHYDRATE

(Short Communication)

J. A. HILL, C. B. MURPHY AND G. P. SCHACHER, *Anal. Chim. Acta*, 24 (1961) 496–497

SEPARATION OF NIOBIUM AND TANTALUM BY N-BENZOYL-N-PHENYLHYDROXYLAMINE

(Short Communication)

A. K. MAJUMDAR AND B. K. PAL, *Anal. Chim. Acta*, 24 (1961) 497–498

VOLTAMMETRIC DETERMINATION OF ANTIOXIDANTS AT THE WAX-IMPREGNATED GRAPHITE ELECTRODE

(Short Communication)

E. BARENDRECHT, *Anal. Chim. Acta*, 24 (1961) 498–499

THE CHARACTERISATION AND DETERMINATION OF NITROGENOUS ORGANIC BASES IN MIXTURES WITH AMMONIUM REINECKATE

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(Received October 11th, 1960)

Ammonium reineckate has been used for the isolation, characterisation and determination of nitrogenous organic bases. It has been applied to the following classes of substances: simple amines[1-3], amino acids[4-11], alkaloids[12-25], antibiotics from *streptomyces fradiae*[26-32], muscarine and related derivatives[33,34], proteins[35], quaternary ammonium compounds[36-38], synthetic bases such as narcotics[23,39,40], antihistamines[17,23], sulphonamides[23], anaesthetics[41], and many other organic bases[42-48]. It has also been used for the spectrophotometric determination of the molecular weights of these compounds[23,49].

In spite of the extensive usage of this reagent, it has not yet been utilised systematically to characterise and determine organic bases in mixtures. STRACK AND SCHWANEBURG[50] reported the separation of choline from betaine obtained from animal tissues using this reagent in 1936. The potentialities of ammonium reineckate as a reagent for the separation of organic bases has not been further investigated and it is the object of the present investigation to evaluate the usefulness of ammonium reineckate for this purpose. This must necessarily involve the study of the reaction mechanism between ammonium reineckate and organic bases, a study which should be of considerable value because of the importance of the reaction to the analyst as well as the toxicologist. A preliminary report on this investigation has already been published[51].

EXPERIMENTAL

Formation of reineckates in alkaline media

About 50 mg of a base was added to 50 ml of water and a few drops of ammonia ($d = 0.88$) followed by 30 ml of ammonium reineckate. The precipitate obtained was filtered, dried and recrystallised from 60% ethanol. Piperidine, dimethylamine, trimethylamine, diethylamine and choline gave the expected reineckates when reacted under these conditions. However with pyridine, aniline and caffeine, no reineckates were obtained.

Effects of variation of pH on yields of reineckates of water-soluble bases

Buffered solutions of pH 1 to 12 were prepared according to CLARK AND LUB[52,53].

Ammonium reineckate solution — approximately 3% solution prepared by dissolving 3 g of ammonium reineckate in 100 ml of cold water and filtering through a Whatman No. 1 filter paper and then through a Whatman No. 42 paper. Freshly prepared solutions were used in all these experiments. The bases used were piperidine, pyridine, morpholine, caffeine and nicotine.

Procedure. About 25 mg of the base was added to 30 ml of the buffer solution of the appropriate pH followed by 15 ml of ammonium reineckate solution. The resulting solution was cooled in a refrigerator for 2 h and filtered through a sintered glass crucible with suction. The precipitate was washed with 5 ml of the appropriate buffered solution and then dissolved in acetone. The acetone solution was transferred to a 25-ml volumetric flask, made up to volume and the optical density of the solution was measured at 525 mμ with a Hilger spectrophotometer. The amount of base recovered was calculated by means of the following equation:

$$w = A/\varepsilon \cdot M \cdot 25/1000 \qquad (1)$$

where w = weight of base recovered in mg, A = observed optical density, ε = gram-molecular extinction coefficient of ammonium reineckate, ($\varepsilon_{525\ \mathrm{m}\mu} = 106.5$), and M = molecular weight of the base used in g. The derivation of this formula has already been discussed[23].

For nicotine the precipitate obtained was filtered, dried over phosphorus pentoxide and weighed. Table I shows the recoveries and compositions of the nicotine reineckates

TABLE I

RECOVERY OF NICOTINE AS REINECKATE AT VARIOUS pH

No.	Nicotine mg	pH	Reineckate obtained mg	Cr content of reineckate
1	50	2	246.2	12.92
2	50	2	247.2	12.89
3	50	3	245.8	12.91
4	50	3	246.0	12.86
5	50	4	234.2	12.46
6	50	4	232.5	12.41
7	50	5	177.0	11.24
8	50	5	178.5	11.36
9	50	6	177.0	11.31
10	50	6	177.0	11.25
11	50	7	178.3	11.07
12	50	7	178.6	11.13
13	50	8	150.1	10.97
14	50	8	149.5	10.85
15	50	9	148.5	10.86
16	50	9	148.6	10.77
17	50	11	127.3	10.83
18	50	11	136.2	10.72
19	50	11	121.5	10.69

Theoretical yield for 50 mg of nicotine as the mono-reineckate is 148.3 mg, Cr = 10.81%, and as the di-reineckate is 247.0 mg ,Cr = 12.97%.

obtained. Fig. 1 shows the recoveries for piperidine, pyridine, morpholine and caffeine at various pH.

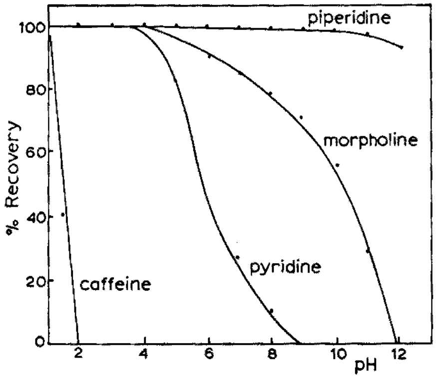

Fig. 1. Recoveries of bases as reineckates at various pH.

Preparation of barium reineckate

A saturated solution of Reinecke's acid (prepared by precipitation from a saturated solution of ammonium reineckate with concentrated hydrochloric acid) was added to a saturated solution of barium chloride. The barium reineckate obtained was recrystallised by dissolution in a minimum quantity of methanol and reprecipitation by the addition of excess of ether. The pure barium reineckate was obtained after two recrystallisations.

	Calcd. for $Ba[Cr(NH_3)_2(SCN)_4]_2$ %	*Found* %
Barium	17.72	17.68
Nitrogen	21.78	21.85

Reaction between barium reineckate and bases in absolute alcoholic solutions

The A.R. ethanol and isopropanol used in these experiments were twice distilled over sodium.

TABLE II

RECOVERIES OF PIPERIDINE AND MORPHOLINE AS THEIR REINECKATES FROM REACTION IN ABSOLUTE ALCOHOLS

Amine	*Amount used mg*	*Ethanol Reineckate obtained mg*	*Cr %*	*Amount used mg*	*Iso-propanol Reineckate obtained mg*	*Cr %*
Piperidine	48.1	204.0	12.75	44.2	207.3	12.93
	43.2	201.3	12.81	43.1	199.2	12.84
Morpholine	53.1	143.2	12.82	57.2	149.2	12.91
	47.2	140.1	12.71	51.0	155.0	12.84

About 200 mg of recrystallised barium reineckate was dissolved in 30 ml of the absolute alcohol and approximately 50 mg of the base was then added. The solution was allowed to stand at room temperature for 3 h, and the precipitate was filtered, dried over phosphorus pentoxide and weighed. The results obtained were shown in Table II. Aniline (pK_b 9.3) and pyridine (pK_b 8.6) gave no precipitates under these conditions.

Formation of reineckates of weak bases

A. Preparation of reineckates of water-soluble bases. About 2 g of the base was dissolved in 20 ml of water and 5 ml of concentrated hydrochloric acid was added to this solution followed by 80 ml of 2% ammonium reineckate solution. The precipitate which was obtained was filtered and recrystallised with 0.1 *N* hydrochloric acid. To prepare urea reineckate 8 g of urea was used. The reineckates of urea, thiourea, acetamide and acetone semicarbazone were prepared in this manner.

B. Preparation of piperine reineckate. About 300 mg of the piperine was dissolved in 15 ml of chloroform in a separating funnel. To this were added 10 ml of 25% hydrochloric acid solution and 80 ml of 2% ammonium reineckate solution. The resulting mixture was shaken thoroughly and the reineckate salt formed was filtered and recrystallised in a minimum quantity of ethanol which was subsequently diluted with 0.1 *N* hydrochloric acid. The dried reineckate salt is yellow but gives a red coloured solution in acetone.

C. Preparation of diphenylamine reineckate. About 200 mg of diphenylamine was dissolved in approximately 5 ml of concentrated sulphuric acid. Approximately 15 ml of water was added slowly to this solution. After cooling the solution, 80 ml of ammonium reineckate was added. The diphenylamine reineckate obtained was recrystallised as described earlier.

Preparation of di-reineckates of nicotine, quinine and thiamine

Procedure 1. Formation in acid media. About 100 mg of the base or its salt was dissolved in 20 ml of *N* hydrochloric acid solution. Excess of ammonium reineckate solution was added and the precipitate formed was filtered and recrystallised by dissolving the precipitate in the minimum quantity of acetone and subsequently diluting this acetone solution with *N* hydrochloric acid. Analyses of the chromium contents of the compounds so obtained showed them to be the di-reineckates of these bases.

Procedure 2. Conversion of mono-reineckates to di-reineckates. An acetone solution of mono-reineckate was added to a solution of ammonium reineckate acidified with *N* hydrochloric acid. On chilling the di-reineckates were obtained.

Preparation of mono-reineckates of nicotine, quinine and thiamine

Procedure 1. Formation in alkaline media. About 100 mg of nicotine, quinine sulphate or thiamine hydrochloride was added to a buffer solution of pH 8.5, followed by 50 ml of ammonium reineckate solution which was added with stirring. The mono-reineckates of these compounds which were obtained after chilling were filtered and recrystallised from 50% acetone solution.

Procedure 2. Conversion of di-reineckates to mono-reineckates. To an acetone solution of the di-reineckate were added two drops of 10% ammonia and excess distilled water. The precipitate obtained was filtered and recrystallised from 50% acetone solution. Pure mono-reineckates of these three compounds were obtained by these two procedures.

Separation of piperidine and pyridine

Weighed quantities of piperidine and pyridine were dissolved in 60 ml of buffer solution of pH 9. To this solution was added 30 ml of ammonium reineckate solution. After cooling for one hour the solution was filtered through a weighed sintered glass crucible under suction. The piperidine reineckate was washed with a few ml of buffered solution, dried over phosphorus pentoxide and weighed.

During the filtration of piperidine reineckate an acid trap containing a few ml of dilute sulphuric acid was used to trap any pyridine that may have volatilised from the filtrate during suction. This sulphuric acid was added to the filtrate which was further acidified with 50% sulphuric acid.

Pyridine was precipitated as the reineckate, filtered and weighed as described above. The recoveries of the bases are shown in Table III.

TABLE III

RECOVERIES OF BASES FROM MIXTURES

No.	*Mixtures*	*Amount added mg*		*Amount recovered mg*	
1	Piperidine–Pyridine	83	147.3	82.6	145.0
2	Piperidine–Pyridine	150.8	38.7	151.2	37.3
3	Piperidine–Pyridine	23.4	15.8	21.9	16.3
4	Codeine–Caffeine	52.4	256.3	51.4	252.7
5	Codeine–Caffeine	21.4	84.3	20.1	80.6
6	Codeine–Caffeine	15.7	482.4	15.2	477.5
7	Codeine–Caffeine	20.2	90.4	18.7	87.7

Separation of codeine and caffeine

Weighed amounts of codeine phosphate and caffeine were dissolved in 40 ml of buffer solution of pH 3.5 with warming. After cooling, 15 ml of ammonium reineckate solution was added, and the solution was cooled to 0° for one hour and filtered. The codeine reineckate was dissolved in acetone and determined colorimetrically by measuring the optical density of the solution at 525 mμ. The filtrate containing the caffeine was made alkaline with sodium hydroxide solution and extracted with chloroform. Evaporation of the chloroform yielded the caffeine which was dried and weighed.

Determination of mixtures of mono- and di-basic compounds

1. Determination of nicotine and pyridine in mixtures. To a 100-ml beaker were added 10 ml of a solution containing nicotine and pyridine, 30 ml of buffer solution of pH 8.5, and 15 ml of ammonium reineckate solution. After chilling for 2 h the solution was filtered through a sintered glass crucible under suction. The precipitated nicotine mono-reineckate was washed with 3 to 5 ml of the buffer solution and dissolved in acetone and 2 ml of 0.1 N hydrochloric acid, and the solution was transferred to a V_0 ml volumetric flask and diluted to mark. The absorption (A_0) of this solution was measured at 525 mμ. The amount of nicotine recovered was calculated from the following formula:

$$w_0 = A_0/106.5 \cdot M_0 \cdot V_0/1000 \qquad (2)$$

where w_0 = weight of nicotine recovered in mg, 106.5 = gram-molecular extinction coefficient of ammonium reineckate in acetone at 525 mμ and M_0 = molecular weight of nicotine in g.

To ascertain the pyridine content of the mixture another 10 ml of the solution was added to 20 ml of N hydrochloric acid solution followed by 25 ml of ammonium reineckate solution. The precipitated nicotine di-reineckate and pyridine reineckate were filtered through a sintered glass crucible, dissolved in acetone, transferred to a volumetric flask of V ml and diluted to mark. The optical density of this solution (A) at 525 mμ was measured and the pyridine content calculated from the following equation:

$$w = (A\,V/V_0 - 2\,A_0)/106.5 \cdot M \cdot V/1000 \qquad (3)$$

where w = amount of pyridine recovered in mg, M = molecular weight of pyridine in g. The recoveries are shown in Table IV.

TABLE IV

DETERMINATION OF MIXTURES OF MONO- AND DIBASIC COMPOUNDS

No.	*Mixtures*	*Amounts added mg*		*Optical densities*		*Amounts recovered mg*	
				A_0	A		
1	Nicotine–Pyridine	10	10	0.250	1.063	9.52	10.43
2	Nicotine–Pyridine	10	10	0.252	1.060	9.55	10.33
3	Nicotine–Pyridine	10	10	0.264	1.071	10.02	10.05
4	Nicotine–Piperidine	10	10	0.776	1.039	10.00	10.03
5	Nicotine–Piperidine	10	10	0.768	1.027	9.85	10.01
6	Nicotine–Piperidine	10	10	0.757	1.030	10.40	9.70
7	Thiamine HCl–Choline	15	10	0.536	0.738	16.00	9.50
8	Thiamine HCl–Choline	15	10	0.530	0.722	15.10	9.60

Volume of acetone used $V_0 = V = 25$ ml in the above experiments

2. *Determination of nicotine and piperidine.* The procedures for the determination of piperidine and nicotine in mixtures were identical to those described earlier. However, at pH 8.5 both nicotine mono-reineckate and piperidine reineckate were formed and in acid media the nicotine di-reineckate and piperidine reineckate were formed.

Hence the nicotine and piperidine contents can be calculated from the following formulae:

$$w_0 = (A\,V/V_0 - A_0)/106.5 \cdot M_0 \cdot V_0/1000 \qquad (4)$$

$$w = [A\,V/V_0 - 2\{(A\,V/V_0) - A_0\}]\;/\;106.5 \cdot M \cdot V/1000 \qquad (5)$$

where w_0 = amount of nicotine recovered in mg, A_0 = optical density of acetone solution of nicotine mono-reineckate and piperidine reineckate at 525 mμ, M_0 = molecular weight of nicotine in g, V_0 = volume of acetone used to dissolve the nicotine mono-reineckate and piperidine reineckate, w = amount of piperidine recovered, A = optical density of acetone solution of nicotine di-reineckate and piperidine reineckate, M = molecular weight of piperidine in g, and V = volume of acetone used to dissolve the nicotine di-reineckate and piperidine reineckate.

Mixtures of thiamine hydrochloride, a di-basic compound and choline, a strongly basic quaternary compound were also determined by the procedures described above and the recoveries are also shown in Table IV.

The isolation of strychnine from highly decomposed cadavers

About 300 g of human liver from an authenticated case of strychnine poisoning was left to stand at room temperature for one week after which it was finely cut, treated with 10% tartaric acid and extracted with 75% ethanol with warming. The alcoholic solution was filtered and the filtrate evaporated. This residue was taken up with 75% alcohol, filtered and again evaporated. The residue was dissolved in water acidified with 0.1 *N* hydrochloric acid, filtered and extracted with ether to remove any acidic or neutral materials that might be present. The aqueous layer was made ammoniacal, transferred to a separating funnel and extracted with chloroform. The ammoniacal aqueous layer was kept for later treatment.

To the combined chloroform extracts were added 20 ml of buffer solution of pH 11 and 5 ml of ammonium reineckate solution. Some insoluble reineckates were formed at the interface between the water and the chloroform layers. The chloroform layer was separated and washed with water. Half of the chloroform extracts was evaporated and subjected to the usual colour and crystal tests. The remaining chloroform was extracted with 0.1 *N* hydrochloric acid. This acid solution was made alkaline and extracted with chloroform. The chloroform was evaporated and the residue was dissolved in 95% ethanol. The spectral curve of this ethanolic solution is shown in Fig. 2 and is identical to that of pure strychnine.

Ammonium reineckate solution was added to the ammoniacal aqueous layer from above and more precipitate was obtained. The precipitate was recrystallised from aqueous acetone mixture; its molecular weight was determined spectrophotometrically[23] and was found to average 78. This indicates that the isolated bases were mostly ptomaines and not any of the common alkaloids since the latter have molecular weights which are generally greater than 150.

DISCUSSION OF RESULTS

Reaction mechanism

The formation of the reineckates has been hitherto carried out in acidic aqueous media and the reaction between amine salts and ammonium reineckate has been postulated to proceed according to the following equation[1,39]:

$$B\cdot HX + NH_4[Cr(NH_3)_2(SCN)_4] \rightarrow NH_4X + BH\cdot[Cr(NH_3)_2(SCN)_4] \qquad (6)$$

This equation however is applicable to reactions between amine salts and ammonium reineckate only and does not explain some of the reactions between certain free bases and ammonium reineckate in aqueous alkaline media. It has been observed that certain bases form reineckates in alkaline media while others do not. A closer study of the properties of the bases which react with ammonium reineckate in alkali media revealed that they are strongly basic substances such as piperidine (pK_b 2.8), diethylamine (pK_b 2.5), trimethylamine (pK_b 3.2) and quaternary ammonium compounds such as choline. Dibasic substances formed the di-reineckates in acid media and in alkaline media yielded the mono derivatives. Furthermore, Fig. 1 shows that the yields of the reineckates depend on the pK_b values of the bases as well as on the pH of the reaction media.

These observations suggest that the formation of the reineckate proceeds according to the following pattern. When a basic substance (B) is dissolved in water the following equilibrium exists:

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad (7)$$

With the addition of an ammonium reineckate solution the conjugate acid BH^+ thus formed reacts with the $[Cr(NH_3)_2(SCN)_4]^-$ ions arising from the dissociation of ammonium reineckate, and the relatively insoluble complex is formed:

$$BH^+ + [Cr(NH_3)_2(SCN)_4]^- \rightarrow BH[Cr(NH_3)_2(SCN)_4] \qquad (8)$$

The removal of the conjugate acid BH^+ as the insoluble reineckate disturbs the equilibrium represented by eqn. (7) and more conjugate acid is then formed to replace that removed. It is obvious therefore that in an aqueous solution the formation of the reineckate complex depends on the formation of the conjugate acid BH^+ from the base B.

The extent to which the equilibrium as represented by eqn. (7) exists, depends on the strengths of the bases as well as on the pH of the reaction media, and the equilibrium constant is given by

$$K_b = [OH^-]\cdot[BH^+]/[B] \qquad (9)$$

In logarithmic notation eqn. (9) becomes

$$\log [B]/[BH^+] = pK_b + pH - 14 \qquad (10)$$

The reaction between ammonium reineckate and quaternary ammonium compounds as choline is one of substitution thus

$$R_4N\cdot X + NH_4[Cr(NH_3)_2(SCN)_4] \rightarrow RN\cdot[Cr(NH_3)_2(SCN)_4] + NH_4X \qquad (11)$$

and this reaction is independent of the pH of the reaction media. This is true with choline which forms a reineckate even in a 5% sodium hydroxide solution. The reaction in strongly alkaline media is not recommended because the ammonium reineckate decomposes rapidly under these conditions.

Reaction between bases and barium reineckate in absolute alcoholic solutions

Since alcohols possess protogenic properties[54] the base-alcohol equilibrium is

$$B + ROH \rightleftharpoons BH^+ + RO^- \qquad (12)$$

From a study of the reineckate formation of piperidine, morpholine, pyridine and aniline it was found that equilibrium (12) is dependent on the pK_b values of the base present. With strong bases such as piperidine and morpholine the equilibrium proceeds almost completely to the right. With weak bases such as pyridine and aniline the equilibrium lies to the left.

Since the formation of reineckates under these conditions is dependent on the pK_b values of the bases this procedure can be used for the separation of bases. Ammonium reineckate can be used in place of barium reineckate.

Separation of bases with ammonium reineckate

Eqn. (10) predicts the possibility of using ammonium reineckate for the separation of organic bases by varying the pH of the reaction media to values which will be favourable or unfavourable for the formation of a particular reineckate if the pK_b values of the compounds are known. Since the formation of the reineckates depends entirely on the formation of the conjugate acid BH^+ the ideal condition would be to have the term $\log [B]/[BH^+]$ in eqn. (10) equal to a negative value, although a value of +1 may be permissible depending on the solubility of the particular reineckate derivative formed. A clearer picture of the reaction can be obtained by considering the specific cases of piperidine (pK_b 2.8) and pyridine (pK_b 8.6) at pH 9. In the case of piperidine at pH 9

$$\log [B]/[BH^+] = 2.8 + 9 - 14 = -2.2$$

$$\log [B]/[BH^+] = 3.8$$

that is

$$[B]/[BH^+] = 6.3/1000$$

This shows that more than 99.4% of the piperidine exists as the conjugate acid BH^+ and hence the possible formation of piperidine reineckate in alkaline media of pH 9.

Similarly, it can be shown that at pH 9 about 99.7% of the pyridine exists as the free base B, hence pyridine fails to form a reineckate at this pH. However, at pH 2 more than 99.9% of the pyridine exists as the conjugate acid BH^+ which explains the formation of pyridine reineckate in acid media.

Satisfactory recoveries were obtained for the determination of mixtures of (*a*) pyridine and piperidine and (*b*) codeine and caffeine as shown in Table III where the bases were isolated and determined. With mixtures such as (*a*) nicotine and pyridine, (*b*) nicotine and piperidine and (*c*) thiamine hydrochloride and choline, the bases were not isolated but conditions could be chosen which favoured the formation of the mono- or di-reineckates of the dibasic substances, thus making it possible to estimate bases in such mixtures. The recoveries for such mixtures are shown in Table IV.

Eqns. (2) and (3) are of general application for the determination of mixtures of a dibasic compound and a moderately weak monobasic compound, whilst eqns. (4) and (5) can be applied to the determination of mixtures of a dibasic substance and a strong monobasic compound.

Formation of mono- and di-reineckates of dibasic substances

With a knowledge of the reaction mechanism it is possible to control the conditions for the formation of mono- or di-reineckates of dibasic compounds. The dibasic substances can be treated as a mixture of two bases with different pK_b values and the mono- or di-reineckates of nicotine (pK_{b1} 6.2, pK_{b2} 10.9), quinine (pK_{b1} 6.0, pK_{b2} 9.7) and thiamine hydrochloride had been successfully prepared by varying the pH of the reaction media. With dibasic compounds the nature of the reineckates formed depends on the pH of the reaction media. At certain pH values, mixtures of mono- and di-reineckates of nicotine were obtained (Table I). It is important therefore to form the derivatives under the proper pH conditions, otherwise the results obtained can be very misleading.

Although the formation of mono- and di-reineckates of nicotine, quinine and thiamine hydrochloride is reversible, that is

$$\text{mono-reineckate} \underset{\text{alkaline}}{\overset{\text{acid}}{\rightleftharpoons}} \text{di-reineckate}$$

this is not generally true with reineckates of other dibasic compounds. The di-reineckates of many antihistamines yielded the mono-reineckates when recrystallised from

TABLE V

REINECKATES OF BASES

Reineckates	*Decomp. temp. uncorr.* °C	*Cr content* Calc. %	*Cr content* Found %
Quinine (mono)	145–149	8.09	8.21
Quinine (di)	216	10.82	10.90
Thiamine (mono)	148–149	8.93	8.96
Thiamine (di)	160–162	11.51	11.51
Nicotine (mono)	184–185	10.81	10.92
Nicotine (di)	160–162	12.97	12.81
Piperidine	198–202	12.90	12.84
Morpholine	175–177	12.80	12.91
Pyridine	198–202	13.02	13.16
Caffeine	137	10.10	9.93
Diethylamine	260–262	13.24	13.21
Dimethylamine	273–274	14.25	14.36
Triethylamine	200–207	12.35	12.43
Diphenylamine	146–149	10.65	10.70
Acetone semicarbazone	136–140	11.71	11.36
Acetamide	136–138	13.75	13.52
Thiourea	138–140	13.16	13.07
Urea	121–122	13.75	12.35 12.51
Piperine	147–149	8.63	6.81 6.55

60% ethanol and no di-reineckates could be obtained from their mono-reineckates. This was attributed to the instability of these di-reineckates to heat and ethanol[23].

Preparation of reineckates of weak bases

Very weak bases such as urea (pK_b 13.8), piperine (pK_b 8.8) and diphenylamine have been reported not to form any reineckates[1] but eqn. (10) suggested that reineckates of these bases should be obtainable if the reaction were carried out at a very low pH. The reineckates of these three substances, together with those of thiourea, acetamide and acetone semicarbazone, were then prepared by this procedure. The chromium contents of the reineckates agreed with the theoretical values with the exceptions of urea and piperine reineckates (Table V). The low chromium contents of these reineckates are being further investigated.

Isolation of strychnine from highly decomposed cadavers

One of the main problems which confronts every toxicologist is the separation of poisons from putrified organs. Many of the substances produced during putrefaction of cadavers resemble alkaloids in their reactions towards general reagents and certain ptomaines resemble well-defined alkaloids even with special reagents[55]. BRIEGER[56] has described a method for the isolation of certain ptomaines from human cadavers using an alcoholic mercuric chloride solution as the precipitating reagent, but it is obvious that this reagent cannot be used in toxicology for the same purpose, because mercuric chloride will also precipitate many of the wanted alkaloids. The isolation of strychnine from highly putrified human livers using the proposed procedure gave satisfactory results and the high purity of the isolated alkaloid is demonstrated by the spectra shown in Fig. 2.

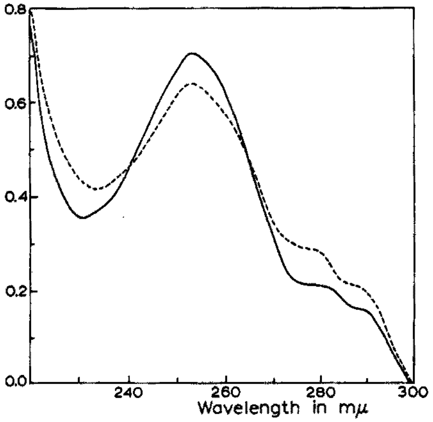

Fig. 2. Spectra of strychnine. ———, the pure strychnine, 2 mg/100 ml -----, from liver. Solvent, 95% ethanol.

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SUMMARY

The reaction between nitrogenous organic bases and ammonium reineckate was studied and was found to depend on the basicity of the bases and the pH of the reaction media. An expression is given which relates the dissociation constant pK_b of a base and the pH of the reaction; when the pK_b of a base is known the pH required for the complex formation can be calculated. The conditions for the formation of reineckates of very weak bases together with the formation of mono- and di-reineckates of dibasic substances are given. The separation of bases whose pK_b values are sufficiently far apart and the determination of mixtures of mono- and dibasic substances were effected by pH adjustment of the reaction media. The isolation of strychnine from putrified human livers is also described.

RÉSUMÉ

L'auteur a effectué une étude sur l'identification et le dosage des bases organiques azotées, en utilisant comme réactif le reinéckate d'ammonium. Quelques séparations sont décrites. Une méthode est également proposée pour l'extraction de la strychnine de cadavres, dans des cas d'empoisonnement.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Trennung und Bestimmung organischer Stickstoffhaltiger Basen mit Reinecke Salz sowie über die Isolierung von Strychnin aus der Leber stark verwester menschlicher Leichen.

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OPTIMUM "COOLING TIME" TO MINIMIZE INTERFERING ACTIVITY IN NON-DESTRUCTIVE ACTIVATION ANALYSIS

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INTRODUCTION

In quantitative non-destructive analysis for an element by neutron irradiation followed by γ-ray spectrometry, the error and detection limit depend on interfering γ-rays to a great extent. As a means of reducing the interference, a choice of a proper length of "cooling time" can be considered. Therefore, the relation between cooling time and the extent of interference has been examined theoretically. In this study, for convenience, the γ-ray of unit energy emitted from a nuclide formed (neutron-induced nuclide) to be determined*, is likened to a "signal", and the interfering γ-ray to a "noise". Thus, the purpose of the work was to discover how to choose a cooling time to make the "signal-to-noise ratio" large. The signal-to-noise ratio under consideration is in the adequately restricted range of γ-energy.

The case when the signal-to-noise ratio is varied by the choice of cooling time is, of course, limited to the case when the half-life of an interfering nuclide is different from that of the nuclide to be determined.

DERIVATION AND RESULTS

In any radionuclide formed the ratio of the emission rate of a γ-ray to the amount of the element which includes the parent of the radionuclide is given by

$$\frac{A_p^\gamma}{W} = N_A f \frac{\sigma_{ac} K}{M} \gamma_p \{1 - e^{-(\ln 2)t/T}\} e^{-(\ln 2)\theta/T}$$

where

A_p^γ = emission rate for an unconverted γ-ray (sec^{-1}),
W = the weight present of the element (g),
N_A = Avogadro's number,
f = flux density of neutrons (cm^{-2} sec^{-1}),
σ_{ac} = isotopic cross section for the neutron activation of a naturally-occurring, parent nuclide, *i.e.*, target isotope (cm^2),
K = fractional abundance of the parent nuclide,
M = chemical atomic weight of the element,
γ_p = fractional abundance of an unconverted γ-ray,
t = irradiation time (sec),
T = half-life of the nuclide formed (sec),
θ = time elapsed after irradiation, *i.e.*, the "cooling time" (sec).

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* The determination of the nuclide formed leads to the determination of the element which is, in most cases, the final purpose in activation analysis.

(Eqn. (1) can be obtained by substituting the quantity $(\ln 2)/T$ for λ in the equation given by Boyd[1] and eliminating the quantities t', A_t' and A_∞ in the resultant equation by putting $t' = \theta$, $A_t' = A_p^\gamma/\gamma_p$, and $A_\infty = N_A f W \sigma_{ac} K/M$).

For convenience it is assumed that the probability for the appearance of one interfering nuclide is equal to the probability for the appearance of another interfering nuclide, and that the counting time is set sufficiently short compared with the cooling time.

Since the species of an interfering nuclide cannot usually be foreseen, the amount of $(\sigma_{ac}K/M)\gamma_p$ in eqn. (1) cannot be forecast for the interfering nuclide. In this situation the only method to be adopted is to adjust the amount of the latter part of eqn. (1):

$$\{1 - e^{-(\ln 2)t/T}\}\, e^{-(\ln 2)\theta/T} \tag{2}$$

By inserting a suitably chosen value for θ the value of formula (2) may be made smaller for any interfering nuclide than for the nuclide to be determined. Such a value of θ, which is, so to speak, an optimum cooling time, can be expressed in terms of irradiation time, as can be deduced from formula (2), and therefore, it is necessary that both irradiation time, t, and cooling time, θ, are chosen properly. In order to compare the various combination of t and θ with each other, the amount of formula (2) has been plotted against T on log-log paper and Fig. 1 has been obtained. From Fig. 1 it is deduced that for a certain half-life there is an optimum cooling time corresponding to an arbitrarily chosen irradiation time, since all the curves in Fig. 1 have points of one maximum. To obtain the optimum cooling time, formula (2) has been put as y and equation $dy/dT = 0$ has been solved. The result is

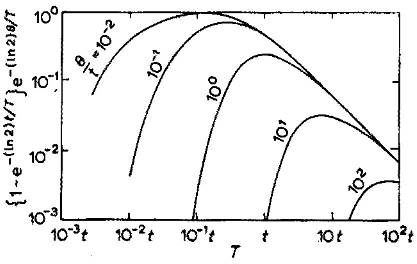

Fig. 1. $\{1 - e^{-(\ln 2)t/T}\}\, e^{-(\ln 2)\theta/T}$ *vs.* T.

$$\theta_0 = \frac{t}{e^{(\ln 2)t/T_0} - 1} \tag{3}$$

where θ_0 is the optimum cooling time, and T_0 is the half-life of a nuclide formed to be determined. According to eqn. (3), θ_0/T_0 has been plotted against t/T_0 on a log–log paper (Fig. 2). The optimum cooling time corresponding to an irradiation time can be readily found by the use of Fig. 2. For example, in activation analysis for hafnium by the formation of hafnium-179 *m* (19 sec), if the irradiation time is set at 60 sec,

t/T_0 becomes 60/19. Hence θ_0/T_0 is read in Fig. 2 as 0.40. Accordingly, θ_0 becomes $19 \cdot 0.40 = 7.6$ sec.

Moreover, from Fig. 1 it is seen that, when θ/t is less than 10°, the smaller is θ/t the smaller is the curvature at the maximum point; accordingly, selectivity for the signal becomes smaller when the half-life corresponding to the maximum point is looked upon as the half-life of the nuclide to be determined, and so the signal-to-noise ratio becomes smaller. It can also be seen that, when θ/t is larger than 10°, the curvature at the maximum is almost constant and larger than the ratio in the first case.

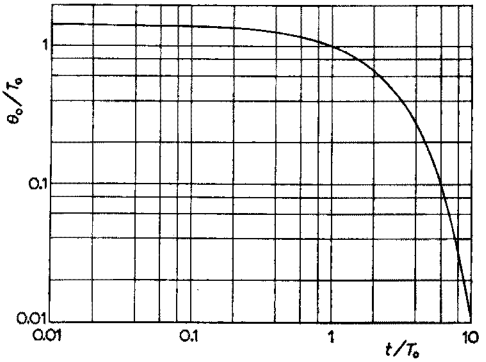

Fig. 2. θ_0/T_0 *vs.* t/T_0

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SUMMARY

In order to choose the best "cooling time" to minimize interfering γ-rays in activation analysis, the "cooling time" has been examined theoretically. There is an optimum cooling time which depends on the time of irradiation and on the half-life of nuclide formed to be determined.

RÉSUMÉ

Après avoir effectué une étude sur le "temps de refroidissement" optimum, dans l'analyse par activation, l'auteur arrive à la conclusion que ce temps optimum dépend de la durée de l'irradiation et de la période du radio-isotope à doser.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über Beziehungen zwischen maximaler Kühlperiode und Störungen durch γ-Strahlen bei Analysen durch Aktivierung. Es wurde festgestellt, dass die maximale Kühlperiode von der Dauer der Bestrahlung und der Halbwertszeit des Isotopes abhängt.

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THE COMPOSITION OF RHODAMINE B CHLOROGALLATE

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Rhodamine B combines, in strong hydrochloric acid solution (6–8 *N*), with the chloroacids of a number of metals to yield intensely coloured red or violet complexes. The complexes formed with Ga^{+3}, Au^{+3}, and Sb^{+5} are soluble in certain organic solvents, such as benzene and chlorobenzene, and have been used as a basis for sensitive photometric procedures for the determination of these elements[1]. Except in the case of antimony[2] no attempt seems to have been made to determine their constitutions. We have found that the gallium complex, in the organic phase, is represented by the formula $(RH)GaCl_4$ ($R =$ rhodamine B). This confirms the formula $(RH)MCl_4$ ($M =$ trivalent metal) suggested by ONISHI AND SANDELL[3] for the complexes of the trivalent elements.

EXPERIMENTAL

Determination of gallium : rhodamine B ratio

Caesium gallium sulphate (10 μg Ga^{+3}) dissolved in 5 ml of 6.5 *N* hydrochloric acid containing 1% w/v titanous chloride was treated with 0.5 ml of a 0.5% aqueous solution of rhodamine B. The gallium was quantitatively extracted by shaking with 8 ml of a 25% v/v solution of carbon tetrachloride in chlorobenzene[4]. After filtration through a glass wool plug, the organic phase was evaporated at 90°. The residue, which consisted of rhodamine B chlorogallate, was treated with water and diluted to 25 ml. Rhodamine B liberated by hydrolysis of the complex was determined by measurement of the optical density of the solution at 555 mμ in a 1-cm cuvette. Quadruplicate experiments gave optical densities of 0.403, 0.405, 0.406, 0.406, average 0.405. Blank runs were also carried out omitting the gallium (optical densities 0.007, 0.009, 0.010, average 0.009). The procedure was calibrated by evaporating to dryness 8-ml aliquots of a solution of purified rhodamine B (10.0 mg/l) in a 1 : 3 mixture of chloroform and chlorobenzene; the residues were diluted to 25 ml with water and gave optical densities of 0.466, and 0.467. These results lead to the ratio of 69.7 μg Ga : 472.8 μg $C_{28}H_{31}O_3N_2Cl$, *i.e.* 1 atom Ga $\equiv$ 0.987 mole rhodamine B.

Attempts were made to recover rhodamine B directly from the organic phase by extraction with water or dilute sodium hydroxide, but although the organic phase turned colourless, no colour was formed in the aqueous phase.

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* This work was carried out in partial fulfillment of the requirements for the degree of Ph.D. (London).

Determination of gallium : chlorine ratio

A solution of rhodamine B chlorogallate in 8 ml of carbon tetrachloride–chlorobenzene mixture was prepared as described above using 20 μg Ga^{+3}. The solvent was evaporated at room temperature in a small basin which was then allowed to stand overnight in vacuo over solid sodium hydroxide. The residue was dissolved in 1 ml of water and transferred to the outer chamber of a Conway microdiffusion cell, the inner compartment of which contained 1 ml of 20% w/v potassium iodide solution. A further 1 ml of water was used for washing the basin. Sulphuric acid (1 ml of 50% v/v) and *ca.* 0.2 g of potassium permanganate were added to the outer chamber. The cell was immediately sealed with a ground glass plate smeared with a mixture of medicinal paraffin and paraffin wax. Chlorine formed by oxidation of the chlorogallate complex was allowed to diffuse into the iodide solution for 6 h. The liberated iodine was titrated with 0.009 N thiosulphate from a micrometer syringe burette. The end-point was detected photometrically using starch as indicator. A blank experiment was run through the whole procedure without the addition of gallium. For standardisation, 2-ml aliquots of a standard sodium chloride solution containing 17.75 mg Cl^-/l were treated with permanganate and acid and diffused in the same manner. It was found that 69.7 μg of Ga was equivalent to 129, 134, 146, average 136 μg Cl $\equiv$ 3.8 μg-at.Cl. Hence in rhodamine B chlorogallate the Ga : Cl ratio is 1 : 4.

SUMMARY

The formula of rhodamine B chlorogallate has been shown to be $(RH)\,GaCl_4$ where R = rhodamine B.

RÉSUMÉ

Le gallium donne avec la rhodamine B, en présence d'acide chlorhydrique, un composé de formule $(RH)GaCl_4$ (R = rhodamine B).

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass der Gallium–Rhodamin B Komplex die Zusammensetzung $RHGaCl_4$ (R = Rhodamin B) hat.

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VOLUMETRIC DETERMINATION OF PERSULPHATE IN SULPHURIC ACID SOLUTIONS BY PERMANGANATE

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As early as in 1897 it was reported by Elbs[1] that perdisulphuric-acid gradually hydrolyses first to permonosulphuric acid and then to hydrogen peroxide. Elbs and Schönherr[2] and later Mugdan[3], and von Bayer and Villiger[4] showed that there is a progressive hydrolysis with the increasing concentration of sulphuric acid with the ultimate formation of hydrogen peroxide. Palme[5] advanced the following mechanism for the hydrolysis.

$$H_2S_2O_8 + H_2O \rightleftharpoons H_2SO_5 + H_2SO_4 \qquad (1)$$

$$H_2SO_5 + H_2O \rightleftharpoons H_2O_2 + H_2SO_4 \qquad (2)$$

The author[6] has confirmed the previous findings and has made some additional observations. It has been found that the amount of hydrogen peroxide produced by the hydrolysis of potassium persulphate reaches a maximum at a particular concentration of sulphuric acid and decreases at higher concentrations of the acid. The amount of hydrogen peroxide produced is equivalent to persulphate in about 12.5 *N* sulphuric acid solution — an observation which led to the present investigation of the quantitative determination of persulphate. To a known volume of persulphate is added the requisite amount of concentrated sulphuric acid and aliquots are titrated with a standard solution of permanganate.

EXPERIMENTAL PROCEDURE

The potassium persulphate and potassium permanganate used were of Merck *p.a.* and B.D.H. quality respectively. Sulphuric acid was of A.R. quality (sp.gr. 1.84) from Orient Scientific Industries, Agra, India. A 5-ml microburette was used and a 5-ml pipette was standardised by the microburette. Persulphate solutions were always freshly prepared by direct weighing and the concentrations were checked by standard methods[7,8].

Preliminary experiments showed that it is best to prepare 50-ml solutions of persulphate in a conical flask for volumetric determination. There are deviations if the total volume is more or less, even though the overall concentration of sulphuric acid is the same. 33.5 ml of the persulphate solution were measured into a 150-ml conical flask and to this were gradually added (0.5 ml at a time) with shaking 16.5 ml of concentrated sulphuric acid (sp.gr. 1.84) from a burette. The mixture was allowed to cool and 5- or 10-ml aliquots were pipetted and titrated with a standard solution of permanganate from a 5-ml microburette. The end-point was marked by the appearance of pink colour which persisted at least for 10 sec. A blank was also run with a solution of sulphuric acid of the same concentration. The readings were usually concurrent and the average of a number of observations was taken.

5-, 10- or 20-ml portions of persulphate solution may also be taken and the requisite volume of distilled water added to make the volume 33.5 ml before adding 16.5 ml of concentrated sulphuric acid. Table I gives a set of typical results.

TABLE I

Conc. of $KMnO_4$ = 0.01968 N, conc. of $K_2S_2O_8$ = 0.02 N; blank reading = 0.02 ml of $KMnO_4$

Mixture *ml*	*$KMnO_4$* *ml*	*Average $KMnO_4$ taken for calculation after deducting the blank* *ml*	*Concentration of $K_2S_2O_8$ found* *N*	*Error* %
5	5.09	5.08	$\frac{0.01968\cdot 5.08}{5} = 0.01999$	—0.005
5	5.10			
5	5.11			
5	5.10			
5	5.10			

Some of the observations using different concentrations of the persulphate and the permanganate are shown in Table II.

TABLE II

Blanks for 0.03921 N and 0.009852 N $KMnO_4$ were 0.01 and 0.04 ml respectively

Concentration of $K_2S_2O_8$ taken *N*	*Reaction mixture titrated* *ml*	*Concentration of $KMnO_4$* *N*	*$KMnO_4$ reqd.* *ml*	*Concentration of $K_2S_2O_8$ found* *N*	*Error* %
0.04	5	0.03921	5.025	0.03941	—1.49
0.04	5	0.01945	10.12	0.03937	—1.56
0.02	10	0.03921	5.11	0.02003	+0.15
0.02	5	0.01945	5.14	0.01999	—0.005
0.02	5	0.009852	10.14	0.01998	—0.10
0.02	5	0.01968	5.08	0.01999	—0.005
0.01	10	0.01945	5.13	0.009978	—0.22
0.005	10	0.01945	2.565	0.004989	—0.22
0.005	10	0.009852	5.07	0.004995	—0.10
0.004	10	0.01945	2.06	0.004006	+0.15
0.002	10	0.01945	1.03	0.002003	+0.15
0.002	10	0.009852	2.025	0.001995	—0.25
0.001	20	0.01945	1.03	0.001002	+0.20

DISCUSSION

The percentage error in most cases is ±0.2 or less and hence the method can be recommended for a quick and direct determination of the persulphate. As has been said before peroxide is obtained by the progressive hydrolysis of persulphate according to the reactions (1) and (2). At higher concentrations of the acid, however, the amount of hydrogen peroxide produced decreases probably because of its decomposition. Table III gives the deviations from the correct result at acid concentrations in the neighbourhood of the recommended one.

TABLE III

Conc. of $KMnO_4$ = 0.01968 N, overall conc. of $K_2S_2O_8$ = 0.02 N, total volume of reaction mixture = 50 ml, reaction mixture titrated = 5 ml

H_2SO_4 ml	*$KMnO_4$ ml*	*Error %*
18.5	5.015	—1.30
18.0	5.03	—1.00
17.5	5.055	—0.50
17.0	5.08	—0.005
16.5	5.08	—0.005
16.0	5.08	—0.005
15.8	5.07	—0.20
15.7	5.03	—0.60
15.5	5.00	—1.60

This table shows that the best acid concentration for the formation of hydrogen peroxide from persulphate is provided by 16.5 ml of concentrated sulphuric acid in 50 ml of solution. At lower concentrations of the acid, the amount of peroxide is less but increases with time, while at higher concentrations, the amount decreases with time. Within the acid concentration range 16–17 ml of concentrated sulphuric acid, there is no change in the amount of hydrogen peroxide even after 72 h. Further it was found that the method is suitable only when the total volume of the reaction mixture is 50 ml. Table IV shows the percentage error for solutions of different volumes, though identical in overall acid concentration.

TABLE IV

Conc. of $KMnO_4$ = 0.01968 N, overall conc. of $K_2S_2O_8$ = 0.02 N, volume of reaction mixture titrated = 5 ml

Total volume of reaction mixture ml	*H_2SO_4 ml*	*$KMnO_4$ required for 5 ml of reaction mixture ml*	*Error %*
20	6.6	4.59	—9.60
30	9.9	5.04	—0.80
40	13.2	5.07	—0.20
50	16.5	5.08	—0.005
60	19.8	5.06	—0.40
100	33.0	4.96	—2.40

Heating or diluting the reaction mixtures does not alter the amount of hydrogen peroxide. It is also interesting to note that the method fails if persulphate is added to the acid solution. Only approximately a quarter of the hydrogen peroxide is formed if the addition of the reactants is reversed. In this case the maximum amount of peroxide is formed at a higher acid concentration (22.5 ml of concentrated sulphuric acid in 50 ml solution), but this corresponds to only 95% of the persulphate.

There is a 5% contraction in the total volume as a result of mixing sulphuric acid with the persulphate solution and there is a 5% decomposition of persulphate or hydrogen peroxide or only 95% persulphate is converted into hydrogen peroxide. However, it is only by chance that the contraction is equal to the decomposition. Hence the method is suitable only under following limitations.

(*1*) The total volume of the reaction mixture should be 50 ml.

(*2*) Sulphuric acid should be added last.

(*3*) 5-, 10- or 20-ml samples should be titrated against the permanganate and not the whole of the reaction mixture.

It may also be mentioned that the persulphate can be determined in a similar manner iodometrically in 10.8 *N* H_2SO_4 when the whole of the persulphate is present in the form of Caro's acid.

SUMMARY

The determination of persulphate in a *ca.* 12.5 *N* sulphuric acid solution by direct titration with permanganate is described. The results are satisfactory but the conditions are critical.

RÉSUMÉ

Une méthode est proposée pour le dosage volumétrique des persulfates, par titrage direct au moyen de permanganate, en présence d'acide sulfurique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Persulfaten durch direkte Titration mit Permanganat in Gegenwart von Schwefelsäure.

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IODIMETRIC DETERMINATION OF CARBON DISULPHIDE

STUDY OF THE EFFECT OF pH

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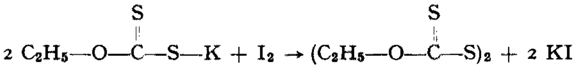
Iodimetric determination of carbon disulphide was first proposed by Delachanal and Mermet[1]; alkali xanthate is formed and the mixture is acidified with acetic acid and titrated directly with standard iodine solution in presence of starch. The reaction is:



$$2\,C_2H_5{-}O{-}\overset{\overset{S}{\|}}{C}{-}S{-}K + I_2 \rightarrow (C_2H_5{-}O{-}\overset{\overset{S}{\|}}{C}{-}S)_2 + 2\,KI$$

Gastine[2] suggested that the titration should be carried out in neutral or slightly alkaline solution and recommended the addition of excess sodium bicarbonate after acidification with acetic acid. Rupp and Krauss[3] also recommended the use of bicarbonate, although their data showed that more iodine was then consumed than in acidified medium. Halban and Kirsch[4] showed that the reaction was not affected by excess of bicarbonate, but was greatly influenced by most organic solvents. The method was reported as inaccurate by André[5].

More recently, Matuszak[6] studied the reaction and confirmed that high results are obtained in presence of excess of bicarbonate (owing to the rapid disappearance of the blue end-point). Avoidance of excess bicarbonate, cooling of the solution in an ice bath, and the use of fresh alcoholic potash solution for the preparation of xanthate gave satisfactory results.

It is obvious that the reaction must depend greatly on the pH of the titrated solution, and that, to obtain quantitative results, it must be carried out under precisely defined conditions. In acid medium, there will clearly be a tendency for the xanthate to decompose and the extent of decomposition is influenced by the hydrogen ion concentration. On the other hand, if the solutions are neutralized (after acidification) with sodium bicarbonate, high results are obtained, presumably owing to the consumption of some iodine by the dixanthogen formed as a result of the primary (forward) reaction. No quantitative data on the kinetics of this reaction have been published, but it appears that the reaction would be accelerated with increase of pH.

The present study was intended to clarify the effect of acidity on the decomposition of xanthate and also whether this decomposition can be retarded sufficiently by using acetate as a buffering agent in place of excess bicarbonate. It is shown that if the titration is carried out within a narrow pH-range in acetic acid–acetate buffered solutions, satisfactory results are obtained and the reaction can be utilized for accurate determinations of carbon disulphide.

EXPERIMENTAL

The accurate weighing of the carbon disulphide presented some difficulties and the following procedure was finally adopted. First a small amount of alcoholic potassium hydroxide was weighed in a weighing bottle. About 0.2 g of carbon disulphide (pure reagent quality) was added and the bottle was reweighed. It was noted that during the time interval, the alcoholic hydroxide itself lost some weight. A large number of experiments showed that if the same amount of alcoholic hydroxide and the same time were taken for weighing, the loss of weight was always the same at room temperature (25–27°). It was thus decided to use 25 ml of 10% alcoholic hydroxide and to carry out the weighing so that the weighing bottle was kept open for *exactly* 30 sec in each experiment. Under such conditions the weight of the carbon disulphide taken had to be corrected by the loss determined by a blank experiment.

The contents of the weighing bottle were washed into 25 ml of 10% alcoholic potassium hydroxide. The excess alkali was neutralized with glacial acetic acid to a phenolphthalein end-point. The solution was then treated with further acid and/or sodium acetate as desired, and diluted to a volume of 250 ml before titration with standard 0.1 *N* iodine solution in presence of starch indicator.

REAGENTS

Fresh alcoholic potassium hydroxide (10%)

This solution was prepared by dissolving 10 g of A.R. potassium hydroxide in 100 ml of absolute alcohol and then cooling the solution in running water.

Iodine solution (0.1 N)

This solution was prepared by dissolving 12.7 g of resublimed A.R. iodine in 100 ml of distilled water containing 40 g of A.R. potassium iodide and then diluting to one litre with distilled water. The solution was standardised against 0.1 *N* $Na_2S_2O_3$ which had been standardised against standard $K_2Cr_2O_7$ solution.

EFFECT OF TIME INTERVAL BETWEEN ACIDIFICATION AND TITRATION

It is quite possible that in acid medium some decomposition of the xanthic acid would take place, and thus cause low results for sulphur; the extent of decomposition would depend on the time taken for the titration. The results presented in Table I show that

TABLE I

EFFECT OF TIME INTERVAL BETWEEN ACIDIFICATION AND BEGINNING OF TITRATION

Time interval (min)	*Corrected wt. of CS_2 taken* g	*Sulphur present* g	*Sulphur found* g	*Error* %
1	0.2254	0.1898	0.1890	—0.5
2	0.2154	0.1814	0.1772	—2.3
3	0.2528	0.2129	0.2078	—2.5
5	0.2742	0.2309	0.2209	—4.4
10	0.2160	0.1819	0.1684	—7.5
20	0.2492	0.2098	0.1803	—14.0

the decomposition does occur to an extent which may vitiate the titration altogether.

In these experiments, the excess alkali was first neutralized with glacial acetic acid (1.8 ml) and then 1 ml of acid was added to give pH 5. The time interval between this acidification and the beginning of the titration was varied; the time taken for the actual titration was kept constant (45 sec). The Table shows that significant results were only obtained when the titration was started within a minute of acidification; otherwise the decomposition was appreciable. It will be seen later that the rate of decomposition is much slower at higher pH.

EFFECT OF pH

Another set of experiments was carried out in which the timing was kept constant (2 min plus 45 sec for titration), but the pH was lowered below 5. The results shown in Table II confirm that the extent of decomposition also depends on the acid concentration and for satisfactory titration, the pH must exceed 5. When no excess of acetic acid is added (pH = 7.7), there is a moderate positive error, which indicates that the pH should be between 5.0 and 7.0.

The results shown in Table III were obtained when the pH was adjusted by adding

TABLE II

EFFECT OF pH

Excess acetic acid added *ml*	*pH*	*(Corrected) wt. of CS$_2$ taken* *g*	*Sulphur present* *g*	*Sulphur found* *g*	*Error* %
0	7.7	0.2018	0.1699	0.1735	+ 2.0
0	7.7	0.2170	0.1826	0.1861	+ 1.9
1	5.0	0.3038	0.2558	0.2483	− 2.9
2	4.7	0.2594	0.2184	0.2077	− 4.9
3	4.5	0.2138	0.1801	0.1692	− 6.1
5	4.3	0.1874	0.1578	0.1435	− 9.1
10	4.1	0.2492	0.2098	0.1691	−19.4

TABLE III

EFFECT OF USING VARYING AMOUNTS OF SODIUM ACETATE IN CONJUNCTION WITH A SMALL EXCESS OF ACETIC ACID

Excess acetic acid used = 1.0 ml for expts. 1 to 6 and 0.5 ml for expts. 7 to 12

Expt. No.	*Sodium acetate used* *g*	*pH*	*Correct wt. of CS$_2$ taken* *g*	*Sulphur present* *g*	*Sulphur found* *g*	*Error* %
1	0	5.0	0.2154	0.1814	0.1772	−2.3
2	2	5.2	0.1828	0.1539	0.1522	−1.1
3	5	5.4	0.2334	0.1965	0.1960	−0.3
4	10	5.6	0.2246	0.1892	0.1890	−0.10
5	15	5.7	0.2152	0.1811	0.1810	−nil
6	20	5.8	0.2238	0.1883	0.1884	+nil
7	0	5.3	0.2456	0.2068	0.2059	−0.4
8	2	5.6	0.2544	0.2142	0.2140	−0.1
9	5	5.8	0.1952	0.1644	0.1653	+0.5
10	10	6.0	0.2656	0.2236	0.2259	+1.0
11	15	6.1	0.2140	0.1802	0.1816	+0.8
12	20	6.25	0.2140	0.1802	0.1832	+1.6

a slight excess of acetic acid (1.0 or 0.5 ml of glacial acetic acid) followed by varying amounts of sodium acetate. It can be seen (see also Fig. 1) that there is no decomposition of xanthate in the pH range 5.7 and 5.8; but a wider pH range from 5.4 to 6.0 can be employed if an error of ±1.0% can be tolerated. Optimally, the titrating solution should be first neutralized (to the phenolphthalein end-point) with acetic acid and then 0.5 ml of acetic acid added together with 2–5 g of sodium acetate before the titration. If more of acetic acid (1.0 ml) is added, more sodium acetate (5–15 g) is required. Under these conditions, carbon disulphide can be satisfactorily determined.

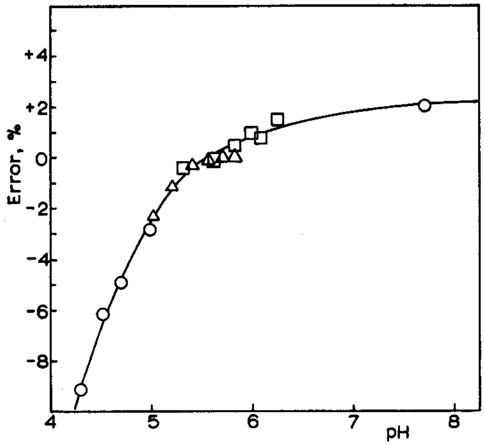


Fig. 1. Effect of pH on iodimetric determination of CS_2. –○– data from Table II; –△– data from Table III (top); –□– data from Table III (bottom).

It has been seen that at a pH of 5.0 or below, a time interval of even one or two minutes between the acidification and the beginning of the titration was unsatisfactory. However, higher pH values in the range of 5.4–5.8 gave satisfactory results for a time interval of two minutes. The data in Table IV show that at pH 5.4 the rate of decomposition is considerably slower and a time interval of even ten minutes can be safely allowed. In these experiments 1 ml of acetic acid and 5 g of sodium acetate were added.

TABLE IV

EFFECT OF TIME INTERVAL BETWEEN ACIDIFICATION AND BEGINNING OF TITRATION AT pH 5.4

Time interval (min)	*Corrected wt. of CS_2 taken* g	*Sulphur present* g	*Sulphur found* g	*Error* %
1	0.2208	0.1861	0.1869	+0.5
2	0.2082	0.1753	0.1760	+0.4
3	0.2144	0.1806	0.1805	nil
5	0.2252	0.1895	0.1882	—0.7
10	0.1840	0.1549	0.1536	—0.9
20	0.2170	0.1827	0.1760	—3.7

RESULTS WITH VARYING QUANTITIES OF CARBON DISULPHIDE

With the optimum conditions indicated above (*i.e.* at pH 5.4) it was shown that amounts of carbon disulphide varying between 0.0060 g and 0.3240 g could be satisfactorily determined by this method (Table V). It should, however, be pointed out that for very small quantities of disulphide, the titrations should be carried out with great care and with a micro-burette.

TABLE V

EFFECT OF VARIATION OF THE AMOUNT OF CS_2

Expt. No.	*Acetic acid needed for neutralization ml*	*Corrected wt. of CS_2 taken g*	*Sulphur present g*	*Sulphur found g*	*Error %*
1	1.9	0.0061	0.0051	0.0051	nil
2	1.9	0.0122	0.0102	0.0102	nil
3	1.9	0.0183	0.0154	0.0154	nil
4	1.9	0.0277	0.0233	0.0233	nil
5	1.9	0.0554	0.0467	0.0472	+1.0
6	1.9	0.1022	0.0860	0.0861	+0.1
7	1.9	0.1227	0.1033	0.1040	+0.7
8	1.9	0.1442	0.1214	0.1222	+0.7
9	1.8	0.1874	0.1578	0.1581	+0.2
10	1.8	0.2082	0.1753	0.1760	+0.4
11	1.8	0.2474	0.2083	0.2070	—0.6
12	1.8	0.2650	0.2231	0.2214	—0.8
13	1.7	0.3240	0.2728	0.2720	—0.3

SUMMARY

The effects of pH and time on the error (due to decomposition of xanthate) involved in the iodimetric determination of carbon disulphide have been studied. A pH range of 5.4 to 5.8 (acetate-buffered) is recommended. Carbon disulphide varying in amount from 0.0060 to 0.3240 g can be determined with an error of ±1.0%.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'influence du pH lors du dosage iodimétrique du sulfure de carbone.

ZUSAMMENFASSUNG

Untersuchung über den Einfluss des pH auf die jodometrische Bestimmung des Schwefelkohlenstoffs.

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DOSAGE COMPLEXOMÉTRIQUE DE CHLORURES, CHLORATES ET PERCHLORATES EN PRÉSENCE LES UNS DES AUTRES

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(Reçu le 31 octobre 1960)

Nous avons décrit une méthode pour la détermination simultanée de chlorates et perchlorates en présence l'un de l'autre[1]. À présent nous présentons la technique pour le dosage complexométrique des chlorures, chlorates et perchlorates dans un mélange. La méthode décrite a l'avantage de pouvoir doser les trois ions en moins de 4 heures, alors que les procédés classiques prennent de 5 à 6 heures. En outre, la précision est très satisfaisante.

FLASCHKA[2] et HUDITZ[3] ont utilisé le complexon-III pour la détermination de chlorures, en dissolvant le précipité de chlorure d'argent dans une solution ammoniacale de nickel–tétracyanure. Les réactions se passent comme suit:

$$2\ AgCl + [Ni(CN)_4]^{-2} \rightarrow 2[Ag(CN)_2]^- + Ni^{+2} + 2\ Cl^-$$

Le nickel déplacé est dosé par voie complexométrique et l'halogène est ainsi déterminé indirectement.

Lorsqu'on ajoute du nitrate d'argent à un mélange de chlorures, chlorates et perchlorates, seuls les chlorures sont précipités. De cette façon, nous pouvons déterminer les chlorures.

Les chlorates doivent être réduits en chlorures pour pouvoir être déterminés par la méthode ci-dessus. Une réduction appropriée est utilisée pour réduire seulement les chlorates, laissant les perchlorates dans leur état initial.

Au moyen d'une réduction plus intense, les chlorates et les perchlorates sont transformés en chlorures et les trois composés du chlore sont précipités en chlorure d'argent.

Les chlorates contenus dans le mélange peuvent être réduits en chlorures en additionnant du sulfate ferreux ou du zinc en poudre à la solution acidifiée (acide acétique). Ces deux procédés de réduction n'affectent pas les perchlorates.

La réduction des perchlorates est effectuée au moyen d'un chauffage du mélange (à l'état solide) avec environ 5 fois le poids de chlorure d'ammonium. Au cours de cette opération, les chlorates sont aussi réduits en chlorures. Le mélange, résultant après réduction ne contient pourtant que des chlorures qui peuvent être précipités par le nitrate d'argent.

Ayant trois précipités de chlorure d'argent, correspondant (1) aux chlorures, (2) aux chlorures et aux chlorates, (3) aux chlorures, chlorates et perchlorates contenus dans le mélange, il est possible de déterminer chacun des composés par voie complexométrique.

Reactifs

Chlorure d'ammonium *(pro analisi)*; solution de sulfate ferreux cristallisé à 10%; solutions de nitrate d'argent à 5% et 0.1%; solution d'acide nitrique à 1%; solution de complexon-III 0.1 *M*; solution saturée de murexide (aqueuse); solution ammoniacale de nickel-tétracyanure 0.1 *M*, obtenue par titrage précis d'une solution de sulfate de nickel 0.1 *M* par une solution de cyanure de potassium 1 *M* après addition d'ammoniaque, le titrage est terminé lorsque l'indicateur (murexide) vire du jaune au violet.

MODE OPÉRATOIRE

Une portion de l'échantillon à l'état de poudre est traitée avec cinq fois son poids de chlorure d'ammonium dans une capsule de platine. On mélange le tout intimement. On recouvre le mélange avec une couche de chlorure d'ammonium et l'on chauffe doucement pendant 1 à 2 h après avoir couvert la capsule avec un verre de montre.

Au cas où l'on utilise une capsule de porcelaine, il faut ajouter au mélange 1 ml d'acide chloroplatinique. On doit veiller à ce que la température du mélange soit au-dessous du point de fusion du chlorure résiduel (sinon on risque d'attaquer les parois de la capsule de platine). On ajoute encore du chlorure d'ammonium et l'on chauffe doucement pendant une demi-heure. On laisse refroidir et l'on dissout les chlorures dans l'eau distillée contenue dans un bécher. On ajoute de l'acide nitrique, puis l'on précipite tous les chlorures à l'aide de nitrate d'argent à 5%. On porte le contenu du bécher à l'ébullition pendant 5 min en prenant soin de couvrir le bécher avec un verre de montre.

On refroidit la solution et l'on filtre sur un Gooch. Le précipité est lavé avec une solution de nitrate d'argent à 0.1%. Il (A) est mis de côte pour être dissous dans la solution de tétracyanure de nickel.

Dans une seconde portion de l'échantillon, les chlorates sont réduits au moyen de sulfate ferreux. La prise d'échantillon est dissoute dans l'eau distillée, puis traitée par 50 ml d'une solution de sulfate de fer(II) à 10%. On chauffe à l'ébullition tout en agitant pendant 15 min. On ajoute l'acide nitrique jusqu'à ce que le sel ferrique basique soit complètement dissous. Les chlorures sont précipités ensuite par le nitrate d'argent. Le précipité (B) est lavé comme dans le cas de (A) puis mis de côté pour le titrage complexométrique.

Une troisième portion de l'échantillon est dissoute dans 100 ml d'eau distillée. On ajoute quelques gouttes d'acide nitrique à la solution jusqu'à réaction acide. Les chlorures sont précipités ensuite par addition de nitrate d'argent. Le précipité (C) est lavé et filtré comme indiqué ci-dessus, puis introduit avec le filtre Gooch dans un bécher de 500 ml contenant la solution ammoniacale de nickel-tétracyanure. On chauffe doucement en agitant jusqu'à dissolution complète du précipité. On ajoute quelques gouttes d'indicateur (murexide) et l'on titre le nickel libéré avec la solution de complexon-III, jusqu'à ce que la couleur de la solution vire au violet. Pour connaître la quantité de Cl^- en mg, il faut multiplier le nombre de ml de complexon-III par 7.0914.

Les précipités (A) et (B) sont traités d'une façon identique et la quantité totale de chlorures est déterminée dans chaque cas. La différence en ml entre les titrages des précipités (B) et (C) donne la quantité de ClO_3^- en mg en multipliant par 16.691.

La différence en ml des titrages des précipités (A) — [(B) + (C)] multipliée par

19.891 donne la quantité en mg de ClO_4^- contenue dans le mélange. Ainsi, on obtient le dosage des trois composés de chlore. Les résultats sont très satisfaisants et la méthode a l'avantage d'être plus rapide que celle de la gravimétrie.

RÉSUMÉ

Une méthode est décrite pour le dosage d'un mélange de chlorures, chlorates et perchlorates par voie complexométrique. Les chlorates et les perchlorates sont réduits à l'état de chlorures au moyen de réducteurs appropriés et précipités ensuite sous forme de chlorure d'argent. Ces précipités (respectifs aux chlorures, chlorates et perchlorates) sont dissous dans une solution ammoniacale de nickeltétracyanure et l'ion Ni^{+2} déplacé par la réaction est titré au moyen du complexon-III. Le chlorure est déterminé indirectement. Trois titrages sont nécessaires pour obtenir les valeurs en mg de Cl^-, ClO^- et de ClO_4^-. Le premier titrage donne la somme des chlorures (après réduction des chlorates et perchlorates). Un second titrage donne la quantité de chlorures après réduction des chlorates seulement et le troisième fournit les chlorures existant dans le mélange. Au moyen de facteurs appliqués aux lectures de burette, on obtient la teneur des trois composés du chlore. La méthode est rapide et sensible. Des essais faits avec des mélanges artificiels ont donné des résultats satisfaisants.

SUMMARY

A method is described for the analysis of a mixture of chlorides, chlorates and perchlorates by complexometric titration. It is based on the partial reduction of chlorates and the reduction of chlorates plus perchlorates respectively; the chloride formed can then be determined.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Analyse eines Gemisches von Chloriden, Chloraten und Perchloraten durch komplexometrische Titration. Das Verfahren beruht auf der partiellen Reduktion des Chlorates bezw. der Reduktion des Chlorates + Perchlorates und Bestimmung des gebildeten Chlorids.

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THERMOGRAVIMETRIC CHARACTERISTICS OF BARBITURIC ACID AND SOME OF ITS DERIVATIVES

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INTRODUCTION

5-Nitrobarbituric acid has been used for the determination of metal cations[1-5] and organic bases[5,6]. The thermogravimetric characteristics of some inorganic and organic salts of 5-nitrobarbituric acid have been given by the authors in previous papers[4,6]. The thermogravimetric characteristics of barbituric acid, dilituric acid (5-nitrobarbituric acid), violuric acid (5-isonitrosobarbituric acid), 1,3-dimethylvioluric acid and barbital (5,5-diethylbarbituric acid) are presented in this paper.

HOTCHKISS AND JOHNSON[7] reported that dibarbituric acid is formed by the loss of one mole of water of composition per two moles of barbituric acid when the latter is heated in glycerol at 170°. The authors have been interested in observing if such a reaction also took place in the solid state.

Dilituric acid, as stated previously, has been used for gravimetric determinations. Thermal stability studies of dilituric acid and the diliturates should prove of value in investigating the proper temperature of heating the diliturates. Such a temperature should be high enough to decompose or sublime any coprecipitated dilituric acid but not high enough to decompose the diliturates.

Violuric and 1,3-dimethylvioluric acid have been used by TAYLOR[8] for the spectrophotometric determination of the alkali and alkaline earth metals. A thermogravimetric study of these acids and salts is reported in this paper to indicate the degrees of hydration as well as the range of stabilities of the anhydrous compounds.

The decomposition of barbital has also been made to study the effect of alkyl substituents in the 5 position on the decomposition.

EXPERIMENTAL

Preparation and purification of the acids

Barbituric acid. Technical grade barbituric acid from Eastman Organic Chemicals was recrystallized from 50% ethanol solution, washed with ether and dried in air overnight.

Dilituric acid. Technical grade dilituric acid from Eastman Organic Chemicals was recrystallized from water and dried in air overnight.

Violuric acid. Technical grade violuric acid from Eastman Organic Chemicals was recrystallized from a 50% ethanol solution and dried in air overnight.

1,3-Dimethylvioluric acid. The method used for the preparation of 1,3-dimethyl-

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violuric acid was essentially that of BILTZ[9] and BILTZ AND HAMBURGER[10] with minor modifications.

Barbital. Barbital, from Eastman Organic Chemicals was used directly without further recrystallization.

Apparatus

An A.D.A.M.E.L. recording thermobalance (Chevenard System) was used to obtain the thermolysis curves. The samples were heated in No. 000 porcelain crucibles, having a volume of about 6 ml.

PROCEDURE

The samples were in the form of powders passing through a 65-mesh sieve. All the compounds were heated in air with the exception of violuric acid, which was run in dry nitrogen, flowing at the rate of 2 l/h. The weights of the samples and the corresponding rates of heating are given in the figures.

In the graphical representations of the thermogravimetric decompositions we have normalized the curves to a percentage change in weight *vs.* temperature. In this way differences in weight of the samples are eliminated and comparison is easier.

Another way of presenting these thermogravimetric decompositions is by a plot of the change in the apparent molecular weight *vs.* temperature. Such plots give a direct measurement of the molecular weight of the fraction decomposing and permit an easy correlation between reactions of similar compounds. An example of such a representation will be shown.

RESULTS AND DISCUSSION

The thermal decomposition curves of barbituric, dilituric and violuric acids are shown in Fig. 1, with the data normalized for percentage decomposition. The thermal decomposition curves of 1,3-dimethylvioluric acid and of barbital are shown in Fig. 2. In Fig. 3 we have the decomposition curves of the same acids as in Fig. 1 but the data in this case have been normalized with respect to changes in the apparent molecular weight. A differential thermal analysis curve for the dehydration and decomposition of dilituric acid is shown in Fig. 4.

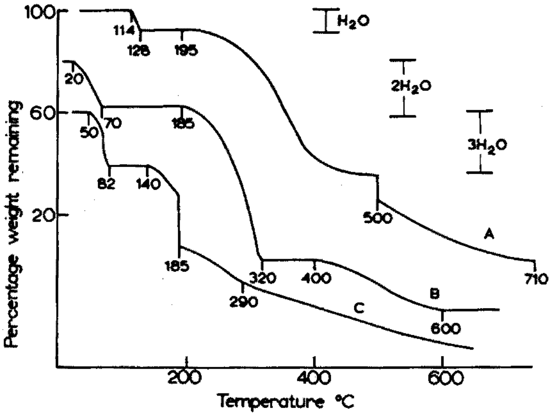

Fig. 1. Thermal decomposition of derivatives of barbituric acid. A. Violuric acid, 45.3 mg heated at 65°/h; B. Barbituric acid, 88.9 mg heated at 65°/h; C. Dilituric acid, 69.3 mg heated at 65°/h.

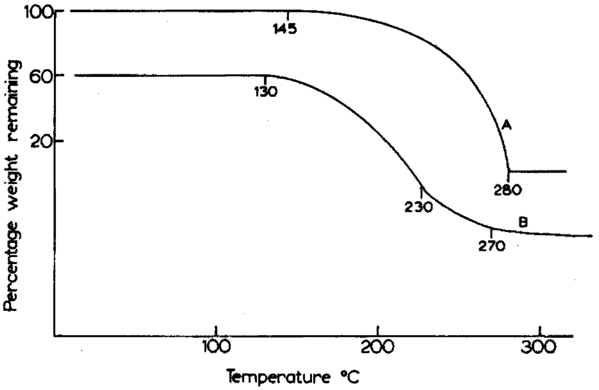

Fig. 2. Thermal decomposition of derivatives of barbituric acid. A. Barbital, 31.8 mg heated at 65°/h; B. 1,3-Dimethylvioluric acid, 40.0 mg heated at 65°/h.

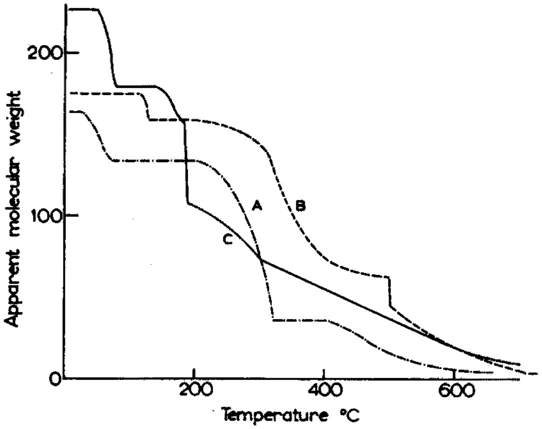

Fig. 3. Thermal decomposition of derivatives of barbituric acid. Curves normalized with respect to changes in the apparent molecular weight. A. Barbituric acid, 88.9 mg heated at 65°/h; B. Violuric acid, 45.3 mg heated at 65°/h; C. Dilituric acid, 69.3 mg heated at 65°/h.

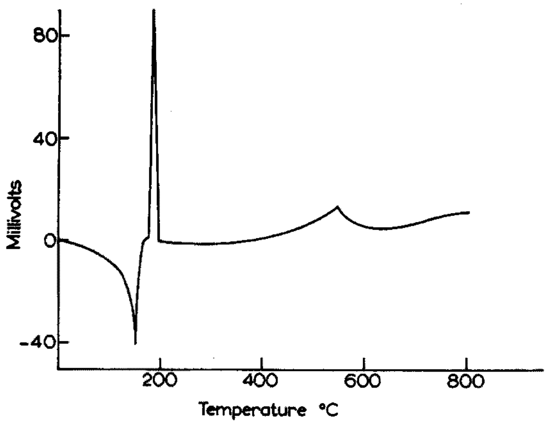

Fig. 4. Differential thermal decomposition of dilituric acid, heated at 300°/h.

Barbituric acid (Fig. 1)

The dehydration of barbituric acid dihydrate began at 20° and terminated at 70°. In spite of the easy dehydration, this water must be water of crystallization since the precipitate had been washed with ether, and normally water of absorption would be removed by this treatment. Anhydrous barbituric acid was stable to 180°. An accelerated loss in weight followed to 320°. From 320° to 400° the residue, representing 22% of the initial weight, was stable. If dibarbituric acid had been formed by a solid state reaction a plateau or a break in the slope of the thermolysis curve would have been observed corresponding to a loss in weight of 27.5%. No such break occurred; we can therefore conclude that dibarbituric acid is not formed by thermal decomposition. The stable residue formed at 320° decomposed slowly to 600° at which temperature no residue was left.

Dilituric acid (Fig. 2)

A trihydrate was formed upon recrystallization from water which dehydrated between 50° and 90°. A more complete discussion of the dehydration of dilituric acid and of the kinetics of this dehydration will be given in a later paper. The anhydrous form of dilituric acid was stable to 140°. A decomposition then was initiated and at 185° dilituric acid exploded, even though there was a low rate of heating. It appears that this explosion will occur under any heating conditions since an explosion also occurred after a certain time, when dilituric acid was heated at a constant temperature of 150°. This is reasonable in view of the high exothermicity of the autocatalytic reaction as shown by the differential thermal curve in Fig. 4. The residue, left after the explosion, decomposed very slowly to 700° where no residue remained.

Dilituric acid is an almost white crystalline compound which dissolves in water to yield a yellow solution with high absorbancy at 380 mμ. The ultraviolet spectrum of this solution was more complex having peaks at 218 and 318 mμ and a shoulder at 237 mμ. It seems that the 218-mμ peak is due to the primary ionization of dilituric acid, while the 318-mμ peak is due to a secondary ionization and is strongly dependent upon the pH of the solution.

The thermal decomposition product of dilituric acid which appeared just before the explosion had a deep red color; it was more easily soluble in water than dilituric acid itself giving a deep red solution with high absorbancy at 520 mμ. This absorption peak disappeared completely within 3 h. The pH of such a solution was about 3 and did not change with the change in color.

If this same decomposition product was dissolved in ethanol then the absorption peak was shifted to 450 mμ and it had a higher stability. The U.V. absorption spectrum of the residue of dilituric acid was only slightly different from that of dilituric acid itself, the peaks having been shifted to 212, 311 and 249 mμ respectively.

Let us note finally that upon evaporation of the faded solution the original red residue was obtained again. This substance dissolved in water forming a red solution which faded on standing in the same manner as the original red solution. This is an indication that the red color is due to an anhydrous form and that the decay is simply a reversible hydrolytic process.

The infrared spectrum of the residue showed the complete disappearance of the 6.75-, 6.95- and 7.00-μ peaks of dilituric acid due to the nitro group.

Violuric acid (Fig. 1)

The monohydrate of violuric acid was quite stable. Dehydration took place between 114° and 130°. The anhydrous form was stable up to 195°. A S-shaped decomposition curve followed to 500° where an explosive like break occurred in the thermolysis curve. The decomposition was terminated at 715°.

1,3-Dimethylvioluric acid (Fig. 2)

This acid did not form a hydrate. Sublimation started at 130° and proceeded without side reactions to 230°, where 28% of the initial weight remained. With the inflection point at 230° the differential change in weight became less accentuated. This can be interpreted as due to coating of the undecomposed dimethylvioluric acid with decomposition product rendering further sublimation difficult. Another break in the curve occurred at 270° indicating a further reduction in the differential change in weight. The residue disappeared completely at 370°.

The decomposition curve of 1,3-dimethylvioluric acid obtained at a rate of heating of 300°/h had an inflection point at 275°. There was a 50% loss in weight, indicating decomposition as the major process whereas sublimation predominated at the slower rate of heating.

Barbital (Fig. 2)

Barbital was also present as the anhydrous compound. It started to sublime at 145° accelerating to 280° where no residue remained.

Comparing the various thermolysis curves it is seen that substitution of an alkyl group for a hydrogen either on the nitrogen or on the 5 carbon makes the resulting compound less stable and with a greater tendency to sublime. The stability of the unsubstituted compound can be attributed to hydrogen bonding within the crystal lattice.

SUMMARY

The thermolysis curves of barbituric acid and some of its derivatives have been determined. Barbituric acid, violuric acid and dilituric acid form hydrates while 1,3-dimethylvioluric acid and barbital are anhydrous. Barbital and 1,3-dimethylvioluric acid sublime before decomposition. The differential thermal analysis for dilituric acid showed a sharp exotherm at 190° indicating a violent explosion.

RÉSUMÉ

Les auteurs ont examiné les courbes de pyrolyse de l'acide barbiturique et de quelques-uns de ses dérivés: acide violurique, acide dilituric, acide diméthyl-1,3-violurique et barbital.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das thermolytische Verhalten von Barbitursäure und einigen Barbitursäurederivaten.

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THERMOGRAVIMETRIC AND MAGNETIC CHARACTERISTICS OF SOME INORGANIC SALTS OF DILITURIC ACID

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INTRODUCTION

The thermogravimetric characteristics of barbituric acid, its 5-substituted derivatives, the organic salts of 5-nitrobarbituric acid and of the diliturates of potassium, magnesium and lead have been reported previously[1-3].

We have determined the degrees of hydration and the thermal decomposition curves of the diliturate salts which have been used for the gravimetric determination of the respective cations (copper[4], nickel[5], cadmium[6], cobalt(II)[7]). We have established the thermal characteristics of the diliturate salts which could be used for the determination of the corresponding cations (iron(II), zinc).

The magnetic susceptibilities of cobalt and iron diliturates have also been investigated to get a better idea of the nature of the bonds formed between the metal cation and the organic portion of the molecule.

EXPERIMENTAL

Reagents and metal diliturates

Dilituric acid solution. The solution used for the preparation of the metal diliturates was an aqueous solution saturated at 25°.

Ammonium diliturate. An excess of dilituric acid solution was added to a 0.1-*M* aqueous solution of reagent grade ammonium chloride. Ammonium diliturate precipitated immediately; it was filtered, washed with water and dried in air.

Rubidium diliturate. Reagent grade rubidium chloride was used for the preparation of rubidium diliturate. The method of preparation was similar to that for ammonium diliturate.

Iron(II) diliturate. An excess of hot dilituric acid solution was added to a 0.1-*M* aqueous solution of recrystallised $Fe(NH_4SO_4)_2 \cdot 6\ H_2O$. The iron(II) diliturate hexahydrate precipitate was filtered, washed with water and dried in air.

Cobalt(II) diliturate. An excess of dilituric acid solution was added to a 0.1-*M* aqueous solution of reagent grade cobalt(II) nitrate from the Allied Chem. and Dye Co. The cobalt(II) diliturate hexahydrate was treated similarly to iron(II) diliturate.

Nickel diliturate. Reagent grade nickel nitrate was used for the preparation of nickel diliturate hexahydrate. The preparation was similar to that of cobalt(II) diliturate.

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Copper dilturate. An excess of a saturated solution of dilituric acid in ethanol (50%) was added to a 0.017-*M* solution of copper nitrate which had been prepared by dissolving copper metal in nitric acid. The copper dilturate octahydrate precipitate which formed was cooled in an ice bath, filtered, washed twice with a 0.02% solution of dilituric acid in alcohol, twice with 95% ethanol and finally with anhydrous ether.

Zinc dilturate. An excess of saturated dilituric acid solution in 50% ethanol was added to a dilute aqueous solution of reagent grade zinc chloride, Allied Chemicals and Dye Co. The resultant mixture was heated, then cooled slowly and finally in ice. Zinc dilturate hexahydrate precipitate was filtered, washed with 95% ethanol and dried in vacuo (water pump).

Cadmium dilturate. An excess of saturated dilituric acid solution was added to a 0.01-*M* aqueous solution of analytical reagent grade cadmium chloride, Mallinckrodt Chemical Works. The resultant mixture was heated, cooled slowly, finally in ice. The cadmium dilturate octahydrate precipitate was filtered, washed with a 0.02% solution of dilituric acid in alcohol and then dried with acetone. The precipitate was further dried in a vacuum desiccator.

Carbon and hydrogen analyses of the above compounds are as follows (see Table I):

TABLE I

Salt	*Calculated*		*Analysed*	
	%C	*%H*	*%C*	*%H*
Rubidium dilturate $RbC_4N_2H_2O_3 \cdot NO_2$ Mol. wt. 257.6	18.65	0.78	18.58 18.39	0.99 0.74
Zinc dilturate hexahydrate $Zn(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 6\ H_2O$ Mol. wt. 517.7	18.56	3.12	17.61 17.50	3.56 3.51
Cadmium dilturate octahydrate $Cd(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 8\ H_2O$ Mol. wt. 600.8	15.99	3.36	15.26 15.46	3.37 3.14
Cobalt dilturate hexahydrate $Co(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 6\ H_2O$ Mol. wt. 511.3	18.79	3.16	18.52 18.27	3.52 3.42
Iron dilturate hexahydrate $Fe(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 6\ H_2O$ Mol. wt. 508.2	18.91	3.18	18.29 17.95	3.68 3.63
Nickel dilturate hexahydrate $Ni(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 6\ H_2O$ Mol. wt. 511.0	18.80	3.16	18.32 18.02	3.40 3.53

Apparatus

An ADAMEL recording thermobalance (Chevenard System) was used to obtain the thermolysis curves. A magnetic susceptibility balance similar to the one described by IHRIG AND CALDWELL[8] was assembled. Due to the low sensitivity of the balance and to the weak magnetic field strength (3700 ± 200 gauss) it was not necessary to enclose the system in a glass container.

Procedure

The samples for the thermolysis determinations were in the form of powders passing through a 65-mesh sieve. They were placed in No. 000 porcelain crucibles, having a volume of about 6 ml. All the compounds were run in air excepting cadmium diliturate which was run in dry nitrogen flowing at the rate of 2 l/h. The weights of the samples and the rates of heating are given in the Figs. In the graphical representation of the thermogravimetric decompositions we have normalized the curves to a percentage change in weight *vs.* temperature.

The method described by SELWOOD[9] was used for calculating the molar paramagnetism χ_M and the permanent effective moment μ_{eff} from the changes in weight of the sample produced by the application of the magnetic field. The magnetic susceptibility balance was calibrated with hydrated ferrous ammonium sulfate. The number of unpaired electrons was related to the permanent effective moment using the expression given by PAULING[10]

$$\mu_{eff} = \sqrt{n(n + 2)}$$

RESULTS AND DISCUSSION

Thermolysis curves

The thermal decomposition curves of ammonium and rubidium diliturates are given in Fig. 1. Alkali metals and ammonium form stable anhydrous salts with dilituric acid.

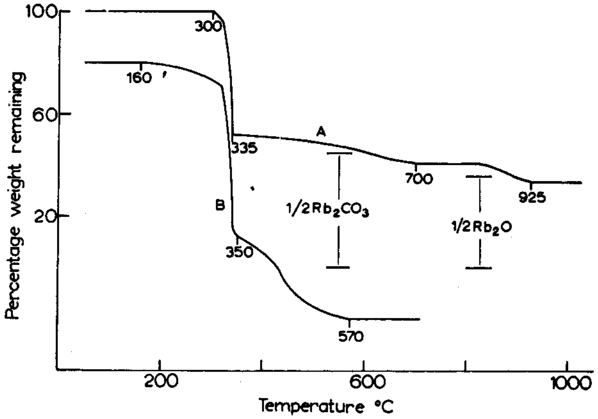

Fig. 1. Thermal decomposition curves. A, Rubidium diliturate, 90.7 mg heated at 300°/h; B, Ammonium diliturate, 131.2 mg heated at 300°/h.

Ammonium diliturate. Anhydrous ammonium diliturate was stable to 160°. A fast decomposition took place up to 350° followed by a decomposition with a S-shaped curve terminating at 570° where no residue remained.

Rubidium diliturate. The decomposition of rubidium diliturate was similar to that of potassium diliturate[3] with the exception that the anhydrous form was stable to 300° and that RbO was formed at 925°.

The thermal decomposition curves of iron(II), cobalt(II), and copper diliturates are given in Fig. 2, while those for nickel, zinc and cadmium dilituràtes are given in Fig. 3.

Iron(II) diliturate. Iron(II) diliturate formed an hexahydrate stable to 80°. A one-step dehydration followed terminating at 200°. The anhydrous compound which resulted was stable to 230°. An explosive decomposition followed to 270° with an inflection point at 350° corresponding to the molecular weight of $FeCO_3$. The final stable residue having the molecular weight of FeO was obtained at 520°.

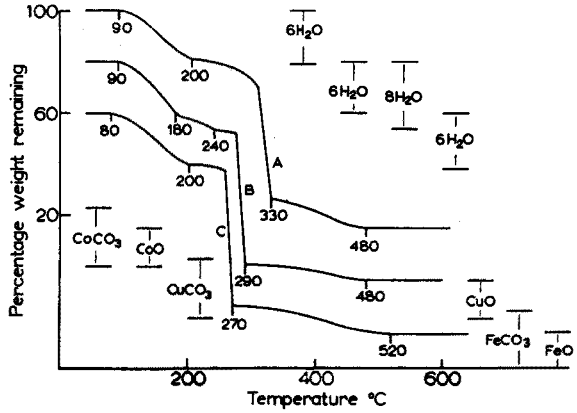

Fig. 2. Thermal decomposition curves. A, Cobalt(II) diliturate, 335.7 mg heated at 300°/h: B, Copper diliturate, 323.1 mg heated at 300°/h; C, Iron(II) diliturate, 273.1 mg heated at 300°/h.

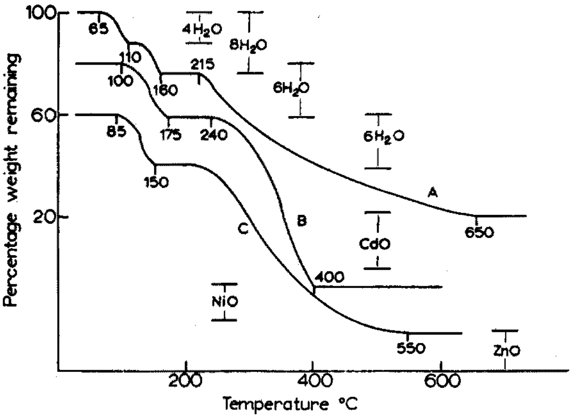

Fig. 3. Thermal decomposition curves. A, Cadmium diliturate, 40.5 mg heated at 150°/h; B, Nickel diliturate, 185.6 mg heated at 150°/h; C, Zinc diliturate, 282.6 mg heated at 65°/h.

Cobalt(II) diliturate. Cobalt(II) diliturate formed an hexahydrate stable to 90°. A one-step dehydration followed terminating at 200°. The anhydrous compound was stable to 230°. An explosion, milder than in the case of iron(II) diliturate, took place to 330° followed by a decomposition with a S-shaped curve giving a residue with a molecular weight corresponding to CoO at 480°. No inflection appeared for an apparent molecular weight corresponding to $CoCO_3$.

Nickel diliturate. Nickel diliturate formed also an hexahydrate stable to 100°. Dehydration took place between 100° and 175° with the resulting anhydrous compound being stable to 240°. A rapid one-step decomposition followed to 400° giving a residue, the molecular weight of which corresponded to NiO.

Copper diliturate. Copper diliturate octahydrate when decomposed at the rate of heating of 300°/h (Fig. 2) was stable to 90° but neither the dihydrate nor the anhydrous forms had any degree of stability. They appeared only as inflection points at 180° and 240° respectively. A very fast decomposition, with explosion, followed to 290°, continued with a slow decomposition until 480° where a stable residue with a molecular weight corresponding to that of CuO remained. When the rate of heating of 65°/h was used instead of 300°/h (Fig. 4) the dehydration of the octahydrate began at 70°, with the intermediate dihydrate being stable between 115° and 150°, and the anhydrous compound being stable between 180° and 190°.

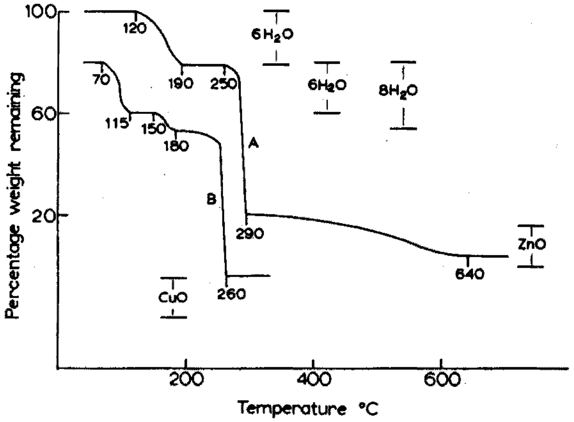

Fig. 4. Thermal decomposition curves. A, Zinc diliturate, 506.7 mg heated at 300°/h; B, Copper diliturate, 348.7 mg heated at 65°/h.

Zinc diliturate. Zinc diliturate hexahydrate when decomposed at the rate of 300°/h was stable to 120°. A one-step dehydration followed to 190°. The carbon and hydrogen analysis of the hydrated zinc diliturate seemed to indicate an octahydrate. This can be due to the different modes of drying prior to analysis or thermolysis. The anhydrous compound was stable to 250°. This was followed by a violent explosion at 290°, in which some of the sample was ejected from the crucible, continued by a decomposition with a S-shaped curve giving a stable residue at 640°. When a rate of heating of 65°/h was used (Fig. 3) the hexahydrate was stable only to 85°, and the anhydrous compound was stable from 150° to 200°. The decomposition of the anhydrous compound was slow leaving at 550° a stable residue with a molecular weight corresponding to ZnO.

Cadmium diliturate. Cadmium diliturate octahydrate was not very stable. An initial partial dehydration took place between 65° and 110°. The tetrahydrate formed was stable to 120°. A second dehydration followed giving anhydrous cadmium diliturate stable from 160° to 215°. The decomposition which followed was very slow and gradual, leaving a stable residue at 650° with a molecular weight corresponding to CdO.

MAGNETIC SUSCEPTIBILITY

Two different determinations of the molar paramagnetism of cobalt(II) diliturate hexahydrate gave values of $\chi_M = 7.5 \cdot 10^{-3}$ and $1.02 \cdot 10^{-2}$ corresponding to μ_{eff} of 4.3 and 4.9 respectively. Cobalt(II) dilurate dehydrated at 192° had a $\chi_M = 5.9 \cdot 10^{-3}$ or $\mu_{eff} = 3.8$ and finally a residue from the decomposition of cobalt(II) dilurate at 250° with an apparent molecular weight of 367 had a χ_M of $7.6 \cdot 10^{-3}$ or $\mu_{eff} = 4.3$. Iron(II) dilurate hexahydrate was found to have $\chi_M = 1.03 \cdot 10^{-2}$ or $\mu_{eff} = 5.0$. A $\mu_{eff} = 4.9$ corresponds to four unpaired electrons while $\mu_{eff} = 3.9$ corresponds to three. The values for the effective magnetic moment obtained for cobalt(II) dilurate and its various decomposition products correspond to approximately three unpaired electrons while the value obtained for iron(II) dilurate corresponds to four. Cobalt(II) has three unpaired electrons in the ionic state (seven electrons in the 3d orbital) while iron(II) has four unpaired electrons (six electrons in the 3d orbital). When these electrons are not paired, as is the case for the above compounds, due to the large positive paramagnetism, then there are no 3d orbitals for bond formation (covalent) and the compounds have to be "essentially ionic"[11]. The water molecules do not prevent the formation of chelates since the number of unpaired electrons remains the same for the anhydrous form. The various metal dilurates are true salts.

SUMMARY

The thermolysis curves of the transition metal dilurates as well as those of copper, zinc, cadmium, ammonium and rubidium have been determined. These dilurates with the exception of ammonium and rubidium dilurates form hydrates. The oxides of the corresponding metals are obtained at relatively low temperatures. Magnetic susceptibility measurements show that these compounds are "essentially ionic" salts.

RÉSUMÉ

Les auteurs ont effectué une étude thermogravimétrique de quelques sels minéraux de l'acide dilitu-rique. Les oxydes correspondants se forment à de relativement basses températures. Des mesures de susceptibilité magnétique ont également été effectuées.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die thermische Zersetzung einiger anorganischer Salze der Dilitursäure (Cu, Zn, Cd, NH_4, Rb). Die Oxydbildung tritt bei relativ niederen Temperaturen ein.

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OBSERVATIONS ON THE USE OF AN ANION EXCHANGE RESIN IN THE DETERMINATION OF AMINOBENZOIC ACIDS, AMINOPHENOLS AND SOME RELATED SUBSTANCES IN BIOLOGICAL MATERIALS

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Although sensitive colorimetric procedures exist for the determination of aminophenols and aminobenzoic acids, difficulties generally arise when applied directly to biological materials, *e.g.* urine. Some preliminary form of separation is often a necessity, not only as an aid to concentration but to eliminate interfering substances and the cation-exchange resin (Dowex 50X12) has been used for this purpose[1].

The present paper is concerned with the use of an anion exchange resin (Dowex 1X10) for a similar purpose. Although there have been reports[2-4] concerning its use in some specialised cases, there is little information with regard to its reaction towards the vast number of organic substances that can occur in some biological materials.

EXPERIMENTAL

Preparation of the column

The resin, Dowex 1X10 (200/400 mesh) was contained in a glass tube fitted with a sintered glass base (Quickfit and Quartz Ltd). The weight of resin used was about 30 g and the dimensions of the operational columns were: height 140 mm, diameter 15 mm.

To ensure that the resin was in the chloride form, before use it was washed with *N* hydrochloric acid and then with water until the pH of the eluate was above 3.0.

Operation of the column

The substances under examination were contained in 100 ml of *N* hydrochloric acid because some biological samples may require a preliminary hydrolysis and this is achieved by heating the acidified sample. Before transferring to the column, the pH of the solution was adjusted to 7.0 by the addition of alkali. The column was then washed with 100-ml quantities of water. Elutions were then carried out with 100-ml quantities of *N*, 5 *N* and 8 *N* hydrochloric acid in turn.

Examination of eluates

Identification in eluates was made by colorimetric, fluorimetric or U.V. spectrophotometric methods. The following colorimetric methods were employed in the assessment of substances referred to in Tables II and III:

(*1*) *o*- and *p*-aminobenzoic and *p*-aminohippuric acids, sulphanilic acid and sulphanilamide: diazotisation with nitrous acid followed by coupling with *N*-(1-naphthyl)-ethylenediamine dihydrochloride[1,5,6].

(*2*) *p*-aminophenol: indophenol pigment formation in the presence of *o*-cresol and ammonia[7].

(*3*) 3-hydroxyanthranilic acid: indophenol pigment formation in the presence of 2,6-dichloroquinone chlorimide[7] or molybdenum blue formation[8].

(*4*) *o*-aminophenol: indophenol pigment formation in the presence of 2,6 dichloroquinone chlorimide[7] or molybdenum blue formation[8].

(*5*) nicotinic acid with cyanogen bromide and *p*-aminoacetophenone[9].

RESULTS

Substances representative of the wide variety that may be encountered in biological materials were transferred to the column in quantities of 1, 2, 5 and 10 mg and the results obtained are summarised in Table I.

TABLE I

THE BEHAVIOUR OF SOME SUBSTANCES WHEN PASSED THROUGH A COLUMN CONTAINING DOWEX 1X10

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(1) Substances not retained

Glutamic acid, aspartic acid, asparagine, cystine, taurine, betaine, trigonelline, methionine, hydroxyproline, citrulline, creatinine, α- and β-alanines, creatine, glycine, 3,4-dihydroxyphenylalanine.

(2) Substances partially retained and removed by washing with water

Nicotinamide, kynurenine, 3-hydroxykynurenine, tyrosine, adrenaline, nor-adrenaline, 3-hydroxytyramine, 5-hydroxytryptamine, $\mathrm{N_1}$-methylnicotinamide, morphine, codeine, strychnine, quinidine.

(3) Substances retained and not removed by water; eluted by N hydrochloric acid

Nicotinic acid, *o*- and *p*-aminobenzoic acids, *p*-aminohippuric acid, sulphanilic acid, sulphanilamide, *o*- and *p*-aminophenols, 3-hydroxyanthranilic acid. Uric acid, phosphate, sulphate.

(4) Substances retained and not removed by water or N hydrochloric acid; eluted by 5 N hydrochloric acid

Kynurenic acid.

(5) Substances retained and not removed by water; not eluted by N, 5 N or 8 N hydrochloric acid

Indoleacetic acid, 5-hydroxyindoleacetic acid, caffeic acid, gentisic acid, gallic acid, ferulic acid, vanillic acid, salicylic acid, hippuric acid, xanthurenic acid, barbituric acid. 3,4-dihydroxybenzoic acid, *o*- and *p*-hydroxycinnamic acids. Phenol, catechol, resorcinol, pyrogallol, vanillin, thymol, phloroglucinol, hydroquinone, *o*-, *m*- and *p*-cresols, α- and β-naphthols.

Amino acids showed no evidence of retention whereas phenols and phenolic acids were retained and could not be eluted by hydrochloric acid as concentrated as 8 *N*.

A large group of substances showed evidence of a variable degree of retention by the resin but could be removed by water alone. With the exception of the alkaloids — strychnine, brucine, codeine and quinidine — 200 ml of water was found to be sufficient to remove such retained substances from the column. In the case of the alkaloids, complete removal from the column required a much greater volume of water.

The remaining group, *i.e.* aminophenols, 3-hydroxyanthranilic acid, aminobenzoic acids, nicotinic acid, sulphanilic acid and sulphanilamide, were completely retained by the column and were not removed by water. These substances could be completely eluted by dilute mineral acid, *e.g.* *N* hydrochloric acid.

TABLE II

THE RECOVERY OF SOME ORGANIC SUBSTANCES

(applied to a column of Dowex 1X10 (30 g) in a solution of 100 ml of *N* hydrochloric acid, the pH being adjusted to 7 by the addition of alkali. Elution with 200 ml of *N* hydrochloric acid)

Substance	*Quantities* *mg*	*Recovery (in 200 ml of N hydrochloric acid eluate)* %
o-aminobenzoic acid	0.5 1.0 2.0	84.5–90.6
p-aminobenzoic acid	0.5 1.0 2.0	86.2–91.6
p-aminohippuric acid	0.5 1.0 2.0	91.6–95.2
o-aminophenol	0.5 1.0 2.0	81.2–86.4
p-aminophenol	0.5 1.0 2.0	82.8–86.2
3-hydroxyanthranilic acid	0.5 1.0 2.0	86.0–89.8
nicotinic acid	0.5 1.0 2.0	83.2–90.2
sulphanilic acid	0.5 1.0 2.0	86.2–94.6
sulphanilamide	0.5 1.0 2.0	87.2–95.8

TABLE III

THE RECOVERY OF SOME ORGANIC SUBSTANCES

(applied to a column of Dowex 1X10 (30 g) in 100 ml of urine + 10 ml of 10 *N* hydrochloric acid, the pH being adjusted to 7 by the addition of alkali. Elution with 200 ml of *N* hydrochloric acid)

Substance	*Quantities* *mg*	*Recovery (in 200 ml of N hydrochloric acid eluate)* %
o-aminobenzoic acid	0.5[a]	83.8 81.8 86.2
	1.0[a]	87.2 90.6 89.2
	2.0[a]	91.2 95.6 93.2
p-aminobenzoic acid	0.5[a]	88.8 86.2 89.1
	1.0[a]	84.2 83.8 90.2
	2.0[a]	90.8 90.6 96.2
p-aminohippuric acid	0.5[a]	91.2 89.8 88.6
	1.0[a]	88.8 91.2 89.2
	2.0[a]	98.2 96.3 94.2
o-aminophenol	0.5[a]	76.3 79.6 80.2
	1.0[a]	79.6 83.2 84.6
	2.0[a]	81.2 83.6 82.2
p-aminophenol	0.5[a]	81.6 83.3 82.6
	1.0[a]	83.6 81.6 82.8
	2.0[a]	81.6 82.3 83.8
3-hydroxyanthranilic acid	0.5[a]	79.2 77.6 80.6
	1.0[a]	81.2 80.6 80.3
	2.0[a]	83.8 84.2 82.6

TABLE III (continued)

Substance	*Quantities mg*	*Recovery (in 200 ml of N hydrochloric acid eluate) %*
nicotinic acid	0.5[a]	89.3 90.2 89.6
	1.0[a]	87.3 85.8 86.3
	2.0[a]	88.6 89.8 85.3
sulphanilic acid	0.5[a]	95.6 94.2 98.6
	1.0[a]	97.2 96.8 94.2
	2.0[a]	94.6 98.6 97.2
sulphanilamide	0.5[a]	92.3 94.6 98.6
	1.0[a]	96.2 95.3 94.6
	2.0[a]	98.6 92.6 91.8
o-aminobenzoic acid	0.5[b]	89.8 93.6 94.2
	1.0[b]	98.6 94.6 92.6
	2.0[b]	93.2 94.6 93.8
p-aminobenzoic acid	0.5[b]	94.6 95.2 93.8
	1.0[b]	94.8 96.2 97.2
	2.0[b]	96.8 98.2 98.6
p-aminohippuric acid	0.5[b]	94.8 95.2 97.2
	1.0[b]	96.8 95.2 94.2
	2.0[b]	96.8 94.3 97.2
o-aminophenol	0.5[b]	76.3 78.3 77.6
	1.0[b]	81.3 83.8 84.6
	2.0[b]	82.6 83.6 81.3
p-aminophenol	0.5[b]	79.6 77.8 81.1
	1.0[b]	83.2 81.6 87.2
	2.0[b]	86.2 79.2 79.8
3-hydroxyanthranilic acid	0.5[b]	79.3 81.3 80.6
	1.0[b]	79.8 83.8 84.6
	2.0[b]	83.2 84.6 81.0
o-aminophenol	0.5[c]	79.3 78.6 77.7
	1.0[c]	81.6 79.2 83.6
	2.0[c]	80.2 83.6 81.2
p-aminophenol	0.5[c]	81.2 77.3 81.2
	1.0[c]	79.2 79.3 80.2
	2.0[c]	80.8 79.3 81.2
3-hydroxyanthranilic acid	0.5[d]	76.3 77.8 79.2
	1.0[d]	81.3 78.4 76.2
	2.0[d]	82.6 83.8 78.3

[a] No additional treatment

[b] The mixture containing the substance in 100 ml of urine + 10 ml of 10 *N* hydrochloric acid was placed in a boiling water bath for 1 h previous to neutralisation and application to the column.

[c] Previous to quantitative determination, the aminophenols were extracted with ether from the *N* hydrochloric acid eluate after the adjustment of the pH to 7 by the addition of solid sodium bicarbonate[1].

[d] Previous to quantitative determination, 3-hydroxyanthranilic acid was extracted with ether from the *N* hydrochloric acid eluate after the adjustment of the pH to 3 by the addition of a saturated solution of sodium acetate.

The quantitative recovery of *o*- and *p*-aminobenzoic, *p*-aminohippuric, sulphanilic, 3-hydroxyanthranilic and nicotinic acids, *o*- and *p*-aminophenols and sulphanilamide was examined. Such were applied to the column in 100 ml of *N* hydrochloric acid after adjustment to pH 7.0 by the addition of alkali. The column was then washed with 200 ml of water which generally proved sufficient to remove loosely retained substances such as kynurenine. Elution was carried out with *N* hydrochloric acid. A volume of 200 ml proved to be sufficient in every case and the results shown in Table II indicate that recoveries were quantitative.

The above experiments were repeated, the substances being applied to the column in 100 ml of urine. Before application, 10 ml of 10 *N* hydrochloric acid were added and the pH adjusted to 7.0 by the addition of alkali. The results shown in Table IIIa indicate that recoveries were quantitative.

In the case of the aminobenzoic acids and the aminophenols, the mixture of urine and hydrochloric acid was heated in a boiling water bath for 1 h, prior to the column technique. This ensures the hydrolysis of all urinary conjugates with the exception of those containing glycine or glutamine. The results shown in Table IIIb indicate that recoveries were quantitative.

The results shown in Table IIIc and IIId indicate that the aminophenols and 3-hydroxyanthranilic acid can be separated from the acid eluates with ether after adjustment to pH 7 (with sodium bicarbonate), and pH 3 (with sodium acetate) respectively[1]. The eluates were not concentrated before this treatment.

DISCUSSION

In earlier experiments columns containing only 3 g of anion (Dowex 1X10) exchange resin were used. Since it was intended to apply the experimental findings to the examination of urine in 100-ml quantities, a column containing about 30 g of resin was adopted. This has proved more than adequate to cope quantitatively with the wide range and variety of substances likely to be present in this volume of urine.

Although the anion (Dowex 1X10) and cation (Dowex 50X12) exchange resins appear to achieve the same purpose, there are some distinct differences which are advantageous when biological materials are under examination.

The cation exchange resin has been successfully applied to the separation of a variety of substances possessing a basic group from human urine as a preliminary to colorimetric analysis. A column containing about 3 g of resin has been used. 100 ml of urine (+ 10 ml of 10 *N* hydrochloric acid) is applied to the column when examination is limited to those substances requiring hydrochloric acid of a normality greater than 1, for example, kynurenine requires 5 *N* hydrochloric acid, to effect elution. Since many of the commoner 'basic' substances, *e.g.* urea, amino acids, are not retained under such conditions, the capacity of the column is not overtaxed by the use of this large volume of urine. 10 ml of urine diluted to 100 ml with water (+1 ml of 10 *N* hydrochloric acid) is applied to the column when examination is made of those substances requiring hydrochloric acid of a normality of 1 or less to effect elution. The capacity of a column of this size has never been found to be overtaxed when the quantity of urine used has been limited to this volume. A column of large size could be used and a larger volume of urine applied but the advantage is negatived by a larger volume of eluant which requires concentration.

After the application of 100 ml of urine to the anion exchange resin, 3-hydroxyanthranilic acid and aminophenols may be recovered in 200 ml of *N* hydrochloric acid eluate. Such represents a relatively slight dilution and the above substances can be recovered by ether extraction (at pH 3 and 7 respectively), concentration of the aqueous phase not being necessary. Eluates obtained from the cation exchange resin are much more dilute and some concentration is necessary before ether extraction is attempted.

The use of the anion exchange resin allows of a speedier separation of these substances from a crude material such as urine. Some *o*-hydroxyamines, *e.g.* 3-hydroxyanthranilic acid, have been shown to be carcinogenic in the free but not in the conjugated form. Since urine is applied to the anion exchange resin at a neutral reaction and elution is speedier, the separation of these two forms is achieved with less risk of hydrolysis of the conjugated form.

The anion exchange resin offers similar advantages to the determination of the aminobenzoic acids in urine. Elution is speedier and eluates are sufficiently concentrated to allow direct determination.

Sulphonamides, if present, would be included but these are not normal constituents of urine. Aminohippuric acids are included but these are minor constituents. Actually a more effective separation of these substances can be achieved by means of the cation exchange resin.

The resolution of the eluate obtained from the anion exchange resin upon the cation exchange resin may be an advantage in many cases.

The separation of alkaloids from acidic radicles by means of the anion exchange resin does not appear to be a practical proposition due to retention problems. Nicotinamide and nicotinic acid may be separated if required. The separation of morphine from *p*-aminophenol, a metabolite of phenacetin, appears to be a practical proposition. This would be of value in toxicological analysis since *p*-aminophenol can seriously interfere with the detection and determination of morphine, and there are relatively few methods for their separation.

SUMMARY

An anion exchange resin (Dowex 1X10) has been studied for the purpose of separating aminobenzoic acids, aminophenols, sulphanilamide and nicotinic acid, preparatory to their determination by colorimetric methods.

RÉSUMÉ

La résine Dowex 1X10 a été examinée en vue de la séparation des acides aminobenzoïques, aminophénols, sulfanilamide et acide nicotinique dans des substances biologiques.

ZUSAMMENFASSUNG

Untersuchung über die Eignung eines Jonenaustauschers zur Trennung von Aminobenzoesäuren, Aminophenole, Sulfanilamid und Nikotinsäure.

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CHROMATOGRAPHIC SEPARATION OF IONS IN PRESENCE OF OXALATE, TARTRATE AND CITRATE, WITH AQUEOUS ETHANOL AS SOLVENT

PART I

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It is well known that complex formation plays an important role in the separation of ions in chromatography. Various workers, including BURSTALL *et al.*[1] and LEDERER AND LEDERER[2], have studied the separation of inorganic ions by paper chromatography using different solvent mixtures with complexing agents. In previous publications[3,4] we have reported studies on the separation of various metal ions in the presence of varying concentrations of complexing agents, with aqueous alcohols as solvent. In this paper we have extended the work to cover the separation of mixtures of 3, 4 or 5 ions and have employed complex formation with oxalate, tartrate and citrate for the separation of ions by ascending filter paper strip chromatography, with aqueous ethanol as solvent.

EXPERIMENTAL

Standard solutions of silver nitrate, lead nitrate, mercurous nitrate, copper nitrate, mercuric nitrate, bismuth nitrate, cadmium nitrate, cobalt nitrate, tin chloride, antimony chloride, arsenic chloride, potassium oxalate, sodium citrate and sodium tartrate were prepared from reagent grade chemicals. The method adopted was the strip filter paper chromatographic technique, as described by GAGE, DOUGLASS AND WENDER[5]. Various concentrations of aqueous ethanol were tried and it was found that 60% ethanol was suitable as solvent. A series of mixtures containing equal concentrations of metal solutions with varying proportions of the complexing agent were prepared, keeping the total volume constant. The ratio of the total molar concentration of the metals to the concentration of the complexing agent added has been expressed as the metal: complexing agent ratio (equivalents of the complexing agent). The mixtures were spotted on Whatman filter paper No. 1 strips. The chromatograms were run at a constant temperature in a room maintained at 27°, the time allowed being 90 min. In mixtures of 3, 4 and 5 ions, the final concentration of each of the metal ions was 0.033 M, 0.025 M and 0.01 M respectively. Mixtures of various metal ions were investigated. The results obtained are summarised in the Table I.

When complexing agents were added, distinct separation zones were obtained, whereas in the absence of complexants the zones were not well-defined. The results

TABLE I

No.	*System investigated (Sequence of separation without adding complexing agents)*	*Complexing agents added (equiv. up to which separation is possible)*			*Sequence of separation (complexing agents added)*
		Oxalate	*Tartrate*	*Citrate*	
1	Pb(II)-Ag(I)-Hg(I)	0.95	0.95	0.70	Pb(II)-Ag(I)-Hg(I)
2	Cd(II)-Hg(II)-Pb(II)	0.32	0.32	0.32	Cd(II)-Hg(II)-Pb(II)
3	Cd(II)-Cu(II)-Pb(II)	0.35	0.35	0.48	Cd(II)-Cu(II)-Pb(II)
4	Cd(II)-Cu(II)-Hg(II)	0.32	0.48	0.48	Cd(II)-Cu(II)-Hg(II)
		—	—	0.8–1.3	Cu(II)-Hg(II)-Cd(II)
5	Cu(II)-Hg(II)-Pb(II)	0.95	0.97	0.97	Cu(II)-Hg(II)-Pb(II)
6	Cd(II)-Cu(II)-Bi(III)	0.35	0.38	0.38	Cd(II)-Cu(II)-Bi(III)
7	Cd(II)-Pb(II)-Bi(III)	0.32	0.32	0.32	Cd(II)-Pb(II)-Bi(III)
8	Cd(II)-Cu(II)-Hg(II) -Pb(II)	0.26	0.24	0.24	Cd(II)-Cu(II)-Hg(II) -Pb(II)
9	Co(II)-Cd(II)-Cu(II) -Hg(II)-Pb(II)	0.50	0.30	0.30	Co(II)-Cd(II)-Cu(II) -Hg(II)-Pb(II)
10	Sn(II)-Sb(III)-As(III)	—	—	0.64	Sn(II)-Sb(III)-As(III)
		0.64–0.96	0.16–0.64	—	Sn(II)-As(III)-Sb(III)

suggest that the complexing property of the ions may be useful in the qualitative separation of these ions from their mixtures. With higher concentrations of the complexing agent than those mentioned, separation is not possible under the experimental conditions. The complexing agent was added to the solution of the metals and not to the solvent as was usually done by previous workers.

SUMMARY

The paper chromatographic separation of Ag, Hg, Pb, Bi, Cu, Cd, Co, As(III), Sb(III) and Sn(II) in mixtures of 3, 4 or 5 of these ions has been studied in the absence and presence of oxalate, citrate and tartrate with aqueous ethanol as solvent.

RÉSUMÉ

Les auteurs ont effectué une étude sur la séparation chromatographique des cations suivants: Ag, Hg, Pb, Bi, Cu, Cd, Co, As(III), Sb(III) et Sn(II). Ils ont examiné également l'influence de réactifs complexants (oxalate, citrate et tartrate).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Trennung von Ag, Hg, Pb, Bi, Cu, Cd, Co, As(III), Sb(III) und Sn(II) durch Papierchromatographie sowie über den Einfluss von Komplexbildnern auf die Trennung.

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QUANTITATIVE CHROMATOGRAPHIC ANALYSIS USING RECTIFIED RADIO-FREQUENCY METHODS

I. LITHIUM, SODIUM AND POTASSIUM

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INTRODUCTION

A series of papers by BLAKE has appeared in this journal in recent years in which a rectified radio-frequency apparatus is described for the detection of spots of electrolyte on chromatography paper. Using this apparatus, which he called "G. G. Blake's Rectified Radio-Frequency Chromatograph Zone Localizer", and which will be referred to henceforth as the "zone detector", he showed that if the galvanometer response be plotted (on the y-axis) against the distance along the paper strip (on the x-axis), then the area under the resultant curve (which he called the "R.Rf. solute distribution/current graph" and which will be referred to as the "detector curve" in this paper) was independent of the shape or area of the spot of electrolyte, but bore a quantitative relationship to the mass of electrolyte[1]. This observation led the present authors to investigate the feasibility of using BLAKE's apparatus for the quantitative determination of spots of ions which had actually been separated by paper chromatography. As the ion spot was in no way changed by the apparatus, the method offered obvious advantages where the separated ions were required for recovery and/or further investigation.

EXPERIMENTAL

Preliminary investigation of several different groups of metal ions showed that where a non-conducting organic solvent mixture was used to develop the chromatogram, a detector curve was obtained in which the background was low and uniform, so that the area of the detector curve corresponding to each ion spot could be determined satisfactorily. On the other hand, when the chromatogram was developed by a solvent mixture containing a conducting compound such as hydrochloric or acetic acid, a detector curve was obtained in which the ion spot curves were superimposed on high and variable backgrounds. Despite all efforts to eliminate this background by heating the developed paper chromatograph in an electric oven or by infra-red lamp, it could not be appreciably reduced, and it was concluded that it was due to a change in the paper itself. Accordingly, it was decided to concentrate further work on the alkali chlorides, which could be separated by non-conducting solvent mixtures.

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Although several different developing mixtures have been described for the chromatographic separation of the alkali chlorides[2,3], none of these was found to give complete separation, and a new mixture was developed for this purpose. This mixture, 3 : 7 (by volume) 2-ethyl hexanol/methanol, gave satisfactory separation of lithium, sodium and potassium chlorides, and was used in all further work. The R_f values for these ions were: $Li^+ = 0.65 \pm 0.04$; $Na^+ = 0.21 \pm 0.03$; $K^+ = 0.06 \pm 0.03$.

Initial quantitative measurements on chromatographs confirmed that the areas under the detector curve for a series of ion spots were proportional to the masses of the respective ions when measured at the same time. However, the same quantity of, say, sodium chloride, gave different detector curve areas on different days, and it was readily established that this variation was dependant on the relative humidity of the atmosphere (Fig. 1). It was therefore clear that although the "zone detector" was very suitable for the determination of the position and limits of chromatograph spots, it could not by itself be used for their quantitative measurement unless ambient humidity were strictly controlled. As this condition was not a practicable one, it was decided to detect and measure the chromatograph spots in two separate steps.

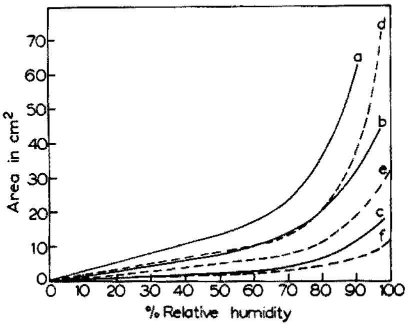

Fig. 1. Dependence of detector curve area on relative humidity of atmosphere. Curves a, b, c: NaCl; 1.09, 0.55, 0.11 mg of Na^+. Curves d, e, f: KCl; 1.09, 0.55, 0.11 mg of K^+.

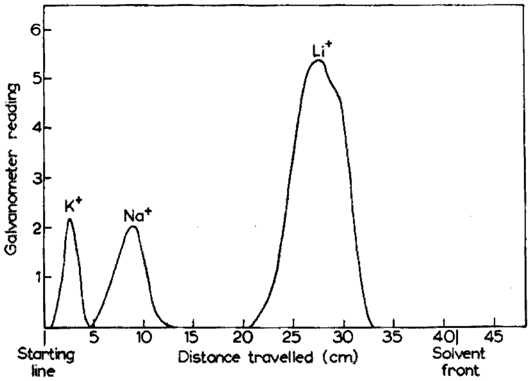

Fig. 2. Typical zone detector curve of mixed potassium, sodium and lithium chlorides.

The position of the ion bands were first determined with the zone detector[4,5], a typical curve thus found being shown (Fig. 2). The bands were then cut out and extracted with a known quantity of distilled water. The impedances of the resulting solutions were measured in a conductimetric tube[4,6], at constant temperature and the mass of the ion found from a calibration curve of Solution impedance/Ion concentration for that particular ion (Fig. 3).

The determination of the quantity of alkali metal ions by this method was convenient, since the apparatus of the zone detector could be used merely by substituting a different electrode system. It should be noted, however, that the zone detector placed no constraint at all on the method of determination of the quantity of ions in the zones it detected. Thus spots of easily hydrolysed ions could be first located by the zone detector, then extracted with dilute acid and determined, say, colorimetrically or by chelometric titration. It would moreover appear that the earlier difficulty encountered, *i.e.* the high and variable background of the detector curve obtained when the chromatogram was developed with a solution containing hydrochloric or acetic acid, should be overcome by the separation of detection and measurement of the ion spots into two independent steps, unless the quantity of ion in a spot were too small for identification against the background.

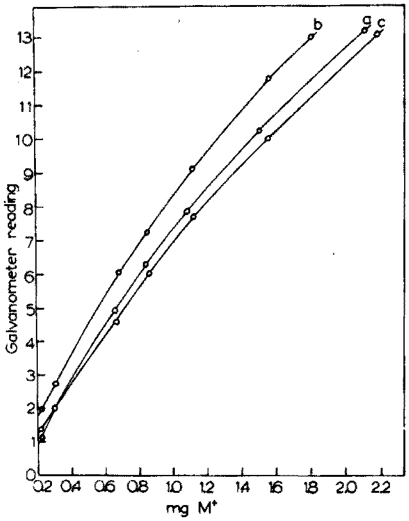

Fig. 3. Calibration curves of solution impedance at 20° plotted against ion concentration. Curve a: Li^+ in 85 ml; curve b: Na^+ in 25 ml; curve c: K^+ in 20 ml.

Materials

Sodium chloride: 1.74 M solution (contained 40 mg Na^+ per ml). A.R. NaCl was dried and the calculated mass weighed out and dissolved.

Potassium chloride: 1.023 M solution (contained 40 mg K^+ per ml). A.R. KCl was dried and the calculated mass weighed out and dissolved.

Lithium chloride: The lithium chloride was weighed as the monohydrate, dissolved, and standardised against standard silver nitrate. It was found to be 5.595 M, *i.e.* 38.8 mg of Li^+ per ml.

Twice-distilled water was used in all cases.

Chromatography paper: Whatman No. 3 chromatography paper gave the best separation. The strips were 5 cm wide and slightly more than 50 cm long. Where less than 1 mg of metal ion was present, strips 2.5 cm wide proved satisfactory.

Developing solvent: This was a 3 : 7 (by volume) mixture of 2-ethyl-hexanol and methanol, and was used without special purification.

The galvanometer used with the zone locator and conductimetric tube was a Pye "Scalamp" galvanometer of sensitivity 177 mm/μA. The results in Table I were obtained using a sensitivity setting of X 0.01, (*i.e.* 1.77 mm/μA).

PROCEDURE

The metal chloride solutions were placed on a pencil line about 3 cm from one end of each strip of paper and dried. The small volumes required were obtained by using calibrated capillary tubes whose volumes covered the range 8 to 55 µl. For each volume, sixteen chromatograms were prepared, consisting of four of the mixed alkali chlorides and four each of the individual alkali chlorides to provide the standards for the calibration curves. The samples were then chromatographed by upward development for 24 h in large glass tanks. Care was taken to prevent the papers from touching whilst in the tank and afterwards while drying.

TABLE I

(Each result is the mean of four to six separate chromatograms)

Metal	*Mixture No.*	*Vol. of water extract (ml)*	*Mean galv. reading (cm)*	*Max. deviation (cm)*	*mg Li^+ present*	*mg Li^+ found*	*Error (%)*
Li^+	1	85	13.02	0.08	2.13	2.12	− 1
	2	85	10.18	0.12	1.52	1.52	< 1
	3	85	7.85	0.25	1.20	1.20	< 1
	4	85	6.36	0.04	0.84	0.86	+ 2
	5	85	5.05	0.05	0.67	0.68	+ 1
	6	85	2.05	0.20	0.30	0.30	< 1
	7	85	1.12	0.02	0.21	0.21	< 1
Na^+	1	25	12.70	0.05	1.83	1.80	− 2
	2	25	11.63	0.15	1.57	1.57	< 1
	3	25	9.13	0.18	1.13	1.14	+ 1
	4	25	7.43	0.20	0.87	0.88	+ 1
	5	25	6.19	0.10	0.69	0.71	+ 3
	6	25	3.03	0.30	0.31	0.34	+10
	7	25	2.08	0.38	0.22	0.23	+ 5
K^+	1	20	12.89	0.04	2.19	2.19	< 1
	2	20	10.08	0.20	1.57	1.60	+ 2
	3	20	7.40	0.20	1.13	1.09	− 4
	4	20	6.06	0.16	0.87	0.87	< 1
	5	20	4.72	0.22	0.69	0.68	+ 2
	6	20	2.13	0.17	0.31	0.32	+ 3
	7	20	1.14	0.11	0.22	0.20	−10

The chromatograms were dried thoroughly to remove the developing solvent, as traces of solvent caused irregularities in the detector curve and errors in the impedance measurements. The dried chromatograms were next conditioned for an hour in a tank of about 90% relative humidity, to increase the effective sensitivity of the zone detector. After the separated ion zones were located by the zone detector, they were cut out with scissors, cut into smaller pieces and placed in dry 100-ml conical flasks. The requisite amount of distilled water was then pipetted in; this amount varied for each of the alkali metals, but was initially found by experiment so that the galvanometer readings were on the scale. It is recommended that the volume be not less than 20 ml.

The flasks were then well shaken and placed in the constant temperature bath (20 ± 0.3°), as the solution impedance varied measurably with temperature. When they had reached the temperature of the bath, they were quickly removed and the impedances of the solutions measured with the conductimetric tube, the galvanometer having been first set to zero for distilled water. The mass of metal ion present was then read from a calibration curve prepared in a similar manner.

The results of analysis of the alkali chloride mixtures are given in Table I, and the calibration curves in Fig. 3.

The upper limit of the range of the method was found to be approximately 2 mg of M^+; larger quantities could not be completely separated on the strips of chromatographic paper used. The lower limit of the range was set by the limit of detection of the zone detector; this was found to be 10 µg for K^+ and 200 µg for Li^+ and Na^+, the difference being due to the fact that the K^+ zone was much less spread out than the others. Within these limits the accuracy of the method may be given as

Li^+, 0.2–2 mg with an accuracy of 1%
Na^+, 0.7–2 mg with an accuracy of 1%
K^+, 0.7–2 mg with an accuracy of 2%.

The accuracy is greatest for Li^+ as the impedance measurements depend on the ionic strength of the solution, which will naturally be the greatest for Li for a given number of mg.

Throughout the work, the solvent front was allowed to travel about 48 cm; it was found that a solvent front movement of 42 cm was necessary to effect complete separation.

Semi-quantitative estimation of µg quantities of the metals could be achieved by running simultaneous reference chromatograms of mg quantities, then cutting out portions of the test chromatograph corresponding to the zones detected on the reference chromatograph. The impedance of the aqueous extract was measured as usual, but with the galvanometer on a five times more sensitive setting. Errors were naturally large, being of the order Na^+, 10%; Li^+, 20%; K^+, 30%.

ACKNOWLEDGEMENT

The authors wish to thank the Australian Atomic Energy Commission for the award of a grant in support of this work. One of us (J. A. B.) also wishes to thank the commission for a scholarship.

SUMMARY

The BLAKE Zone Detector has been shown to be a very useful apparatus for the location of ion zones separated by paper chromatography. In the case of the alkali metals, these zones can be estimated by measuring the impedance of their aqueous extract. An alternative method, that of measuring the area under the detector curve, does not provide a practical means of quantitative measurement. A new developing solvent is described for the paper chromatographic separation of lithium, sodium and potassium chlorides.

RÉSUMÉ

Les auteurs ont étudié la séparation chromatographique sur papier des métaux alcalins (LiCl, NaCl et KCl), en utilisant avec succès l'appareil de BLAKE pour la localisation des zones.

ZUSAMMENFASSUNG

Beschreibung einer papierchromatographischen Trennung der Alkalimetalle unter Verwendung des Apparates nach BLAKE zur Lokalisierung der Zonen.

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DETERMINATION OF LEAD IN GASOLINE BY ATOMIC ABSORPTION SPECTROSCOPY

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The determination of lead in gasoline is one which is carried out with great frequency by the petroleum refining industry. The lead content of a gasoline has a very important modifying effect upon the octane value of that gasoline. There is, therefore, no necessity to point out the importance of this determination, both to the producer and to the consumer of this fuel.

As with most methods of analysis, the most important criteria of the procedure are the accuracy and precision, ease of manipulation, speed of carrying out the procedure, and the degree of interference from other elements or compounds likely to be present in the system. The most commonly used methods for this determination are wet chemical analysis, X-ray fluorescence, and flame photometry. In the *wet chemical procedure* the sample is digested and decomposed with acid. The lead is converted to the sulfate and is determined gravimetrically as lead sulfate. This procedure is quite accurate but is time-consuming and requires considerable attention.

X-Ray fluorescence

The advantage of this procedure is that it is very rapid and requires a minimum of preparation of the sample[1]. Its disadvantages lie in the fact that it is costly to install, and subject to errors from variations in the sample. These variations include carbon/hydrogen ratio and sulfur content.

Flame photometry

The flame photometric procedure is rapid and easy to carry out. However, some interference might be expected from change in concentration of the other trace elements present in the sample.

The atomic absorption procedure possesses all the required advantages described earlier, *i.e.*, a minimum of preparation of the sample is required; time for complete analysis, including calculation, is approximately 10 min, the equipment is relatively cheap. Accuracy of the results obtained show that the method is quite reliable and reproducible. Also, the procedure is remarkably free from interference from other elements present; sulfur and nitrogen content in the sample and variation in the carbon/hydrogen ratio caused no interference at the levels normally encountered. Also, the method enjoyed freedom from interference from metals normally encountered in this type of sample.

DISCUSSION

The process of atomic absorption spectroscopy was first demonstrated by WALSH[2]. The principle of the procedure is that metal atoms will absorb at certain well-defined, characteristic wavelengths. This absorption is intense and permits analyses to be carried in the p.p.m. level. The principle advantages of the procedure are *(1)* high degree of sensitivity, *(2)* high degree of freedom from interference by other metals. A schematic diagram of the equipment used for this process is shown in Fig. 1.

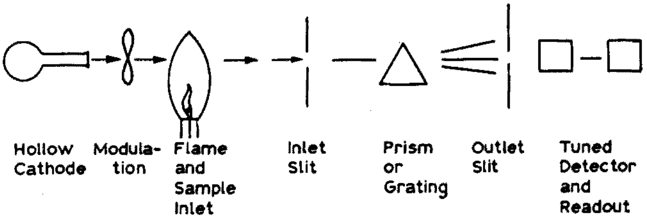

Fig. 1. Schematic diagram of atomic absorption spectrophotometer.

RESULTS

It was determined that lead absorbed strongly at wavelength 2833 Å. At this wavelength the degree of absorption was so intense that the useful range of analysis was limited to between 0 and approximately 70 p.p.m. of lead*. At greater concentrations of lead, the relation between concentration and degree of absorption was on the flat part of the calibration curve and useful analytical results were difficult to obtain. This is shown in the calibration data which illustrate the relationship between concentration of lead and degree of absorption. The results are plotted using the Ringbom relation $K(1 - I_1/I_0) = \log C$. Assuming I_0 is constant, this can be reduced to

$$\log C = K'(I_0 - I_1)$$

where $K = K'I_0$
C = Concentration of metal
I_0 = Intensity of initial signal
I_1 = Intensity of signal after absorption

The most satisfactory working range is between 0 and 70 p.p.m. of lead. To accommodate this limited range, it was necessary to dilute all samples ten-fold. For this dilution, iso-octane was used. Although this dilution necessitated an extra step in the procedure, it had the advantage of virtually standardizing the matrix for all samples. Precision results are shown in Table I.

Interference studies

Solutions were made up to contain 10 p.p.m. of lead and 900 p.p.m. of the metal being studied. Of the following metals examined, no interference was noted. The metals studied were tin, sodium, bismuth, copper, zinc, chromium, iron, and nickel.

Interference from sulfur and nitrogen

The sulfur and nitrogen content of gasoline vary significantly, depending on the

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* 1 ml TEL./gal. = 108 p.p.m. Pb, approximately.

TABLE I

PRECISION RESULTS

Lead conc.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Standard	50	130	220	325	650
Analysis	49.5	128	227	335	647
	49.5	129	219	321	655
	48.5	128	223	321	647
	49.5	129	219	328	655
	50.5	131	219	320	650
	51.0	129	216	320	655
	50.5	130	221	320	650
	50.5	131	221	320	650
		131	217	335	647
		130	216	328	647
		131	217		647
Average	49.4	129.7	219.5	324.5	650.0
	$2\sigma = 1.64$	$2\sigma = 2.5$	$2\sigma = 6.8$	$2\sigma = 13.0$	$2\sigma = 7.0$

source of the crude oil. It was therefore decided to study these elements when present in a high concentration. With sulfur, the compounds carbon disulfide, orthothiocresol, $CH_3C_6H_4SH$, and *n*-butyldisulfide, $C_4H_9SSC_4H_9$, were studied as possible interfering compounds. Diethylamine, $(C_2H_5)_2NH$, was used as the source of nitrogen. To study the effect of interference, an equal quantity of gasoline and possible interfering compound were taken and shaken well. These were then diluted ten-fold and the apparent lead concentration determined. The results are shown in Table II.

TABLE II

INTERFERENCE BY SULFUR AND NITROGEN ON LEAD DETERMINATION

Lead standard p.p.m.	*Apparent analyses interfering compound*		
	Carbon disulfide p.p.m.	*Thiocresol p.p.m.*	*Diethylamine p.p.m.*
50	50	51	51
125	127	127	123
220	220	220	220
325	325	320	330

Sample contained 50% interfering compound, 50% standard. This mixture was diluted ten-fold with iso-octane.

As shown in Table II, there appeared to be no interference from sulfur or nitrogen compounds, even though the compounds were present in an equal volume to gasoline. It is felt that if these elements do not interfere at these high concentrations, they would not interfere at the lower concentrations normally encountered in gasoline analysis. It was concluded, therefore, that the method was free from interference from sulfur and nitrogen. Other studies indicated freedom from interference from halides providing precipitation of the lead did not occur.

EXPERIMENTAL

A schematic diagram of the equipment used is shown in Fig. 1. It was found necessary to include modulation in this equipment in order to eliminate difficulties arising from the emission line of lead which occurs at the same wavelength as the absorption line. Without modulation, the net absorption as detected by the photomultiplier would be subject to the errors present in emission flame photometry.

Source

A lead hollow cathode was used as the source. Its construction is illustrated in Fig. 2.

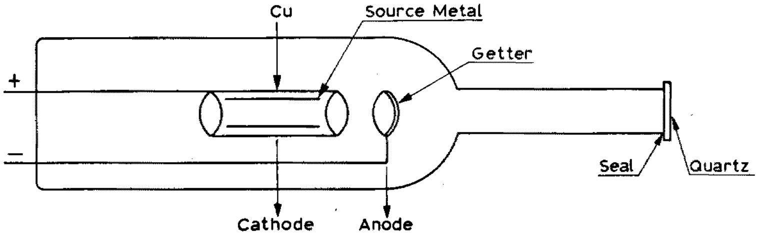

Fig. 2. Design of hollow cathode.

Burner

A standard Beckman flame atomizer burner was used in all cases. The flame was a simple oxy–hydrogen flame.

Monochromator, detector and readout system

A modified Perkin-Elmer Model 13 spectrophotometer was used for this work. Modifications included a chopper operating a 12 cycles/sec and a grating instead of a prism. Although the use of this instrument was quite successful for this application, it is likely that a much simpler instrument embodying modulation of the source and the detector would be quite satisfactory.

PROCEDURE

Calibration

Standard solutions of lead tetraethyl are made up by dissolving in iso-octane. These solutions are prepared to cover the range 0–65 p.p.m. of lead. It is preferable that the standard lead should be in the same form as the sample since different organic compounds of lead may result in a different absorption coefficient and therefore a standard calibration curve may result which would not apply to the samples. The monochromator and detector system are set to read the intensity of the emission line at 2883 Å emitted by the hollow cathode. The unabsorbed signal from the hollow cathode is set to read 100. The source is then shut off, and zero signal is set to read 0. The standard solutions are then aspirated into the Beckman burner in the same way as in flame photometry. The absorption reading, $I_0 - I_1$, is then recorded and plotted in a Ringbom plot where concentration is plotted against $(I_0 - I_1)$, as illustrated in Fig. 3.

Determination of samples

The sample is shaken and 1 ml is accurately pipetted out and placed into a 10-ml graduated flask. Iso-octane (9 ml) is then added until the solution reaches the mark.

The mixture is then well shaken, and the sample poured out and aspirated in the normal way.

The concentration of lead is calculated from the absorbed signal and the calibration curve after suitable correction for dilution.

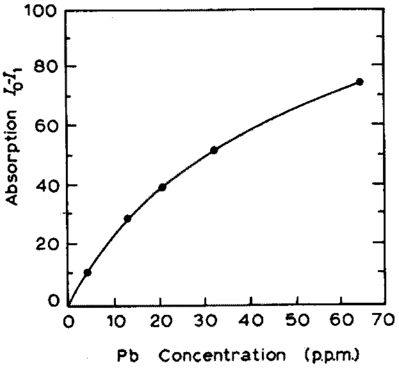

Fig. 3. Calibration curve. Pb concentration (p.p.m.) *vs.* absorption ($I_0 - I_1$).

For subsequent analyses, it must be remembered to set I_0 and zero on the same position on the recorder. This is best accomplished by varying the sensitivity of the detector or the slit widths of the monochromator. For reproducible results it is best not to vary the amperage across the hollow cathode source because of the time necessary to re-attain equilibrium. As a further check a standard solution should be run immediately before a batch of samples requiring analysis. In all cases, a blank should be obtained by running iso-octane alone, and this should be subtracted from the final results.

ACKNOWLEDGEMENTS

The author wishes to thank Esso Standard, Division of Humble Oil & Refining Company, for permission to publish this work.

SUMMARY

A procedure has been developed for the direct determination of lead in gasoline by atomic absorption spectroscopy. This procedure is rapid, does not require expensive equipment, is remarkably free from interference by other trace elements present, and allows considerable variation in the sulfur and nitrogen content of the gasoline. It compares favorably with other existing procedures for this determination, such as X-ray fluorescence, wet chemical methods, and flame photometry.

RÉSUMÉ

Une méthode par spectroscopie d'absorption atomique a été mise au point pour le dosage du plomb dans la gazoline. Ce procédé est rapide; il ne nécessite pas d'appareillage coûteux et il est remarquablement sélectif.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur direkten Bestimmung von Blei in Gasolin durch atomare Absorptionsspektroskopie. Die Methode ist rasch und selektiv.

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THE DETERMINATION OF INDIUM AND THALLIUM IN SILICATE ROCKS BY A COMBINED SOLVENT EXTRACTION AND SPECTROCHEMICAL TECHNIQUE

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INTRODUCTION

The determination of elements of low abundance in geological materials is of considerable interest in geochemistry particularly in those cases (*i.e.* Bi, Tl, Cd, In, etc.) where the concentrations are so low that quantitative determinations are rendered extremely difficult. This problem has to some extent been solved in recent years by the use of neutron activation methods where certain elements can be determined at extremely low concentration levels. A contribution has also been made by the development of techniques depending on the enrichment of elements to the threshold of spectral sensitivity by means of ion exchange followed by spectrochemical analysis. The author has been particularly concerned with the development of anion exchange enrichment techniques, and elements such as Cd, Bi, Tl, Sn, Zn, etc. have been determined in a wide range of geological materials[1-4].

There is however, clearly a place for other methods of separation and enrichment and as has been suggested by SMALES AND WAGER[5] the use of solvent extraction for the solution of the problem is of obvious importance.

In considering methods suitable for the determination of elements at extremely low concentrations in silicate rocks there are certain overriding limitations that must be considered. Of these, by far the most important is that any such method must involve the addition of as few reagents as possible and these reagents must not only be employed in the minimum quantities but must also be easily purifiable, otherwise there is a significant risk of contamination. The author has therefore developed a solvent extraction technique which incorporates simplicity and speed of application with the utmost economy of reagents which are in any case easily purifiable.

IRVING AND ROSSOTTI[6] have investigated the iodo-complexes of the Group IIIb elements and have shown that Tl and In may be extracted quantitatively into ethyl ether from a solution of 1.5 N sulphuric acid and 1.5 N potassium iodide where the hydriodic acid is generated *in situ*. They do not recommend the use of hydriodic acid itself due to its inherent instability. This extraction procedure is however unsuitable for the determination of In and Tl in silicate rocks owing to two factors. Firstly, it has been discovered that even the purest grade of potassium iodide contains significant amounts of Tl, and secondly, it is not easy to obtain a solution of a silicate rock in sulphuric

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acid owing to the formation of insoluble sulphates. A modified procedure was therefore developed in which the rock specimens were finally dissolved in a mixture of 15% (1.7 *N*) hydrochloric acid to which was added sufficient hydriodic acid to make the solution 1.0 *N* with respect to the latter. It was easy to obtain a solution of the rock in this mixture and moreover the reagents were found to be entirely free of In and Tl. These elements were subsequently determined in a suite of eight rocks including the well-known standard granite G-1 and standard diabase W-1 (see FAIRBAIRN *et al.*[7]). Good agreement was obtained not only with the results of other workers for these standard rocks but also with the author's previous work on anion exchange enrichment.

APPARATUS

The spectrochemical determinations were carried out on a large Hilger quartz/glass spectrograph in which the discharge was focussed on the slit by means of a Hilger E 958 quartz lens. A rotating step sector with a transmission ratio of two served to provide a graded series of exposures and the spectra were recorded on Kodak 103-0 blue-sensitive plates in the range 2750 Å to 4680 Å.

EXPERIMENTAL TECHNIQUE

Spectrographic procedure

Since the amounts of the ethereal residues which were to be analysed spectrochemically were exceedingly low (about 5 mg), some form of matrix was necessary to collect the residues and to afford sufficient bulk. Sodium chloride was found to be particularly suitable for this purpose since it not only is readily obtainable in a high degree of purity but also has the property of quenching CN emission during arcing, and hence reduces CN band interference[8] in the region of the most sensitive Tl line at 3775 Å. A further advantage of this matrix is that In, Tl and Bi (the internal standard) are all volatilised by the time that the sodium "D" colour has started to

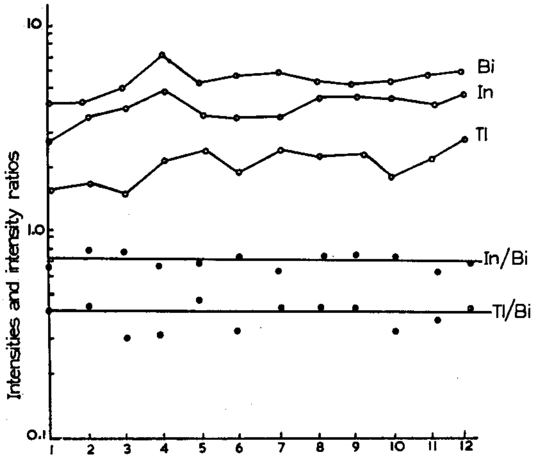

Fig. 1. Replicate arcings of small amounts of Bi, In and Tl showing the efficacy of Bi as internal standard.

wane and cutting off the exposure at this point eliminates much interference from the less volatile elements such as Fe.

A series of volatilisation tests were carried out with various volatile elements conjointly with In and Tl in order to choose a suitable internal standard. Bi was found to be satisfactory for this purpose and in order to assess the reproducibility of replicate arcings, a series of samples containing small amounts of In, Bi and Tl in constant proportions to each other and contained in the sodium chloride matrix were arced at 7 A. The spectral lines measured were: Tl 3775 Å, In 3256 Å and Bi 3067 Å. The samples were loaded into $^3/_{16}''$ graphite electrodes the dimensions of the cavity being 3.2 mm (internal diam) × 5 mm (depth).

The replicate intensities of In, Tl and Bi and the intensity ratios of the line pairs In/Bi and Tl/Bi are shown in Fig. 1.

Standard deviations were calculated and were found to amount to 10.0% for the line pair In/Bi and 16.5% for Tl/Bi. The reproducibility for In can be considered spectrographically satisfactory, whereas that for Tl is only fair.

Extraction of the iodo-complexes of In and Tl into ethyl ether

As has already been stated, the extraction of the iodo-complexes of In and Tl into ethyl ether from a solution in which the hydriodic acid is generated *in situ* with the aid of sulphuric acid is not satisfactory but hydrochloric acid is an excellent medium for the dissolution of silicate rock residues after removal of the silica with hydrofluoric acid. A series of experiments were therefore carried out to measure the percentage extraction of In and Tl from a solution of small amounts of these elements in 15% hydrochloric acid to which varying amounts of hydriodic acid were added. The hydriodic acid concentrations used were 0.2 N, 0.5 N, 1.0 N, and 1.5 N, respectively.

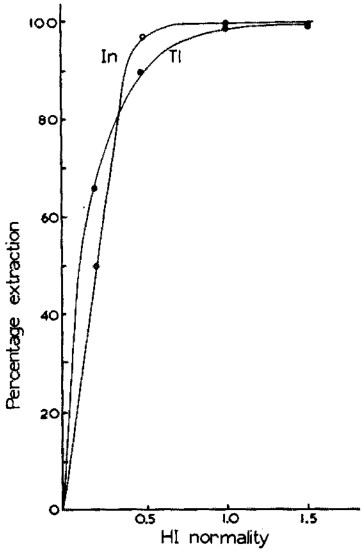

Fig. 2. The percentage extraction of the iodo-complexes of In and Tl as a function of HI normality.

Sulphur dioxide was passed through each solution until the brown iodine colour had disappeared in order to ensure that all iodine was present in the anionic form and that the Tl was present completely in the monovalent state. Each solution was then shaken with an equal volume of ethyl ether which had been previously equilibrated with 15% hydrochloric acid. The aqueous and organic phases were then separated, taken to dryness and the residues collected in the sodium chloride matrix and the In and Tl determined spectrochemically using Bi as internal standard.

In Fig. 2 the percentage extraction figures are shown as a function of hydriodic acid normalities and it will be noted that the extraction of each element increases rapidly to a limiting value of about 99% at 1.0 *N* acid. This acid concentration was taken as the optimum for all future work bearing in mind the desirability of keeping all reagent concentrations down to a minimum.

Determination of In and Tl in silicate rocks

The method whereby the In and Tl concentrations were determined in 8 silicate rocks was as follows: 10-g samples of rock were digested in a 150-ml Teflon beaker with 50 ml of AR grade hydrofluoric acid and 50 ml of AR grade aqua regia[9]. The mixture was taken to dryness in a water bath and the residues were transferred to a borosilicate glass beaker to which 20 ml of sulphuric acid were added followed by heating until all the acid had been removed. The sulphated residues were then dissolved in the minimum quantity of 15% hydrochloric acid and the rock solutions divided into two equal volumes each representing 5 g of the original rock. Each duplicate had a final volume of about 200 ml. Sufficient AR grade hydriodic acid was now added to each solution to adjust the concentration of this acid to 1.0 *N*. Sulphur dioxide gas was then passed through each sample until the iodine colour had disappeared and the In and Tl were then extracted with an equal volume of pre-equilibrated ethyl ether in a 1000-ml separating funnel. Each ethereal extract was taken to dryness and a further 50 ml of 15% hydrochloric acid were added followed by the requisite amount of hydriodic acid. After treatment with SO_2, the trace elements were again extracted with an equal volume of the ether. The purpose of the double extraction was to effectively separate the In and Tl from other interfering elements in particular Fe and also to remove traces of sulphuric acid remaining from the sulphation stage of the procedure. If this acid is present, it is difficult to obtain a satisfactory dry and compact residue for packing into the electrodes due to "creeping" of the acid during the final stages of the technique.

The second ethereal residues were taken to dryness in 50-ml porcelain basins and the iodine removed by adding a few ml of nitric acid. The usual sodium chloride matrix and Bi standard were added in solution form and the residues were again taken to dryness. The samples were loaded into graphite electrodes and arced at 7 A in the wavelength range 2750 Å to 4680 Å.

Working curves were also prepared using amounts of In and Tl ranging from 0.02 to 2.0 μg in steps of 0.02, 0.04, 0.10, 0.20, 0.60 and 2.0 μg in 20 mg of NaCl. Each sample contained in addition 10 μg Bi as internal standard.

A further set of standards was prepared in which the In and Tl were in each case given a double extraction treatment exactly as the 8 silicate rocks. Both sets of standards when plotted on the working curve were indistinguishable from each other and indicated that the extraction procedure was completely effective.

RESULTS

A typical spectrogram (quartz felspar porphiry) is shown in Fig. 3 and it will be noted that the spectral lines are quite strong and clear. The experimental results are summarised in Table I and show gratifying agreement with independent data obtained on G-1 and W-1 by other workers using different experimental methods. The table also shows that good agreement has been obtained with the author's own previous work on anion exchange enrichment.

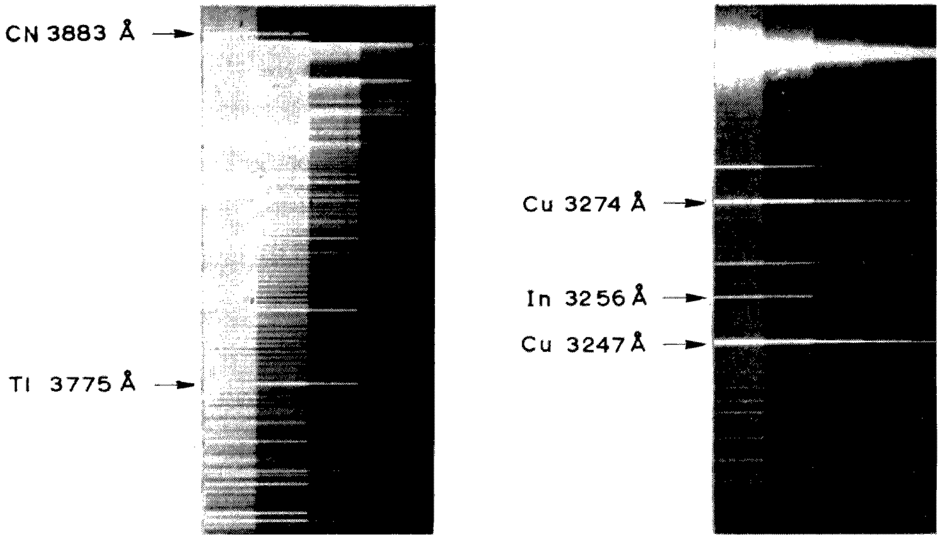

Fig. 3. Spectrogram of ether extract from solution of quartz felspar porphiry showing In and Tl lines.

TABLE I

THE ABUNDANCE OF Tl AND In IN SILICATE ROCKS (DATA FOR Mn ALSO INCLUDED)

Name of rock	*Locality*	*p.p.m. Tl*				*p.p.m. In*		*p.p.m. Mn*
G-1	Westerley, Rhode. I, U.S.A.	1.27[a]	1.30[b]	1.30[c]	1.27[d]	0.042[a]	0.026[e]	210[f]
Quartz felspar porphiry	Paresis igneous complex, S.W.A.	0.71[a]	—	—	—	0.070[a]	—	600[f]
W-1	Centerville, Virginia, U.S.A.	0.21[a]	0.17[b]	0.1[c]	0.11[d]	0.094[a]	0.064[e]	1300[f]
Gabbro	Paresis igneous complex, S.W.A.	0.18[a]	—	—	—	0.120[a]	—	1300[f]
Nepheline syenite	Paresis igneous complex, S.W.A.	0.59[a]	—	—	—	0.266[a]	—	1532[f]
Hortonolite dunite	Lydenburg, Tvl. South Africa	—	—	—	—	0.336[a]	—	5500[f]
Cape granite	Cape peninsula, South Africa	1.30[a]	—	1.40[c]	—	0.070[a]	—	—
Shale	Mouille point, Cape Town, S.A.	0.12[a]	—	0.18[c]	—	0.027[a]	—	—

[a] This paper
[b] MORRIS AND KILLICK[10]
[c] BROOKS, AHRENS AND TAYLOR[1]
[d] VINCENT[11]
[e] SMALES *et al.*[12]
[f] TAYLOR[13]

DISCUSSION

The agreement obtained for the abundance of Tl in G-1 is particularly striking and a figure of 1.29 p.p.m. is suggested with some confidence. Agreement for W-1 is not quite so good but the average of 0.15 p.p.m. for the four sets of data cannot be far from the truth. The author has obtained figures for the abundance of In in G-1 and W-1 which are about 50% higher than the figures obtained by SMALES *et al.*[12] by neutron activation, but considering that the two techniques are entirely different and that the concentrations concerned are particularly low, the measure of agreement is quite good. SHAW[14] has pointed out that there is no apparent regularity in the distribution of In in silicate rocks apart from a tendency to be associated with Sn. This has been noted by RANKAMA AND SAHAMA[15] and GOLDSCHMIDT[16] who have however suggested the possibility of an association with Mn since the respective ionic radii are extremely close (Mn^{+2} = 0.81 Å : In^{+3} = 0.80 Å). Fortunately, independent abundance data are available for Mn in 6 of the rock samples and an apparently fairly close association between the two elements has been noted in these samples. Fig. 4 shows a log/log plot of In concentrations as a function of Mn concentrations. It is obvious that firm conclusions cannot be drawn from analyses on only six samples but there is no doubt that a further investigation into this apparent association would be of great interest and it should be possible to apply the method described in this paper to the speedy and efficient estimation of In and Tl in a large number of geological materials.

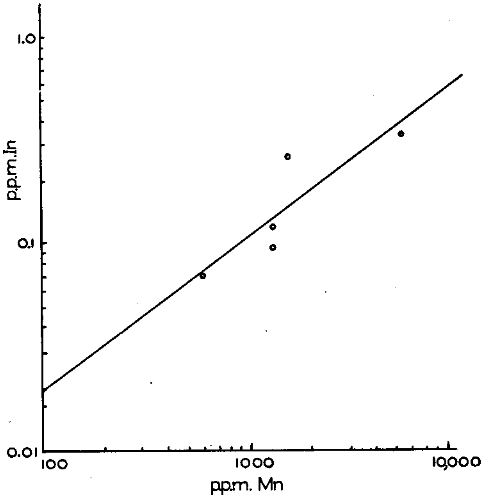

Fig. 4. In concentrations in six silicate rocks expressed as a function of Mn concentrations.

SUMMARY

A technique has been developed for the determination of In and Tl at very low concentrations in silicate rocks. The iodo-complexes of these elements are extracted from the rock silicate into ethyl ether and the ethereal residues are analysed spectrochemically. The optimum working conditions were established by a study of the variation of percentage extraction as a function of hydrogen iodide normality; the reproducibility of the spectrochemical procedure was investigated. In and Tl were determined in eight silicate rocks including standard granite G-1 and standard diabase W-1. Good agreement was obtained with results of other workers for these two rocks and with the author's previous results. The evidence for a In/Mn coherence in silicate rocks is sufficiently strong to warrant further investigations.

RÉSUMÉ

Une méthode est proposée pour le dosage de très faibles quantités d'indium et de thallium dans des silicates. On procède à l'extraction des iodocomplexes de ces éléments, puis à leur dosage spectrochimique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung sehr kleiner Mengen von Indium und Thallium in Silikaten durch Extraktion der Jodo-komplexe mit anschliessender spektrochemischer Bestimmung.

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CONTRIBUTIONS TO THE STUDY OF ORGANIC OSMIUM REAGENTS

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Investigations carried out by various workers on organic reagents for osmium indicate that this element mainly reacts with reagents containing the $>$C=S group. Tshugaeff[1] reported that osmium reacts very sensitively with thiourea. This reaction was used by Sandell[2] for the detection of osmium in meteorites. The reactions of osmium with thiourea derivatives were studied by Steiger[3] who examined 21 derivatives with the general formula $(R_2N)_2CS$. Yoe and Overholser[4] studied the reaction of 60 thiourea derivatives with 78 inorganic ions including osmium and ruthenium. Bardoděj[5] investigated a series of organic reagents and considered the $>$CS group as the functional analytical group for osmium and ruthenium.

Recent work[6] included an investigation of the colour reactions of osmium with two mono-substituted thiourea derivatives, namely: 4-acetylaminobenzaldehyde-thiosemicarbazone and 4-nitrobenzaldehyde-thiosemicarbazone, both reactions being more sensitive than the thiourea method.

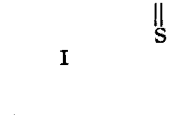
The present paper reports the reactions of osmium with two other mono-substituted thiourea derivatives and with four organic heterocyclic compounds containing the —SH group attached to the ring.

REAGENTS AND PROCEDURE

Reagents

Osmium tetroxide solutions were prepared by dissolving approximately 1 g of OsO_4 in 100 ml of 0.2 *M* sodium hydroxide, the titre of the solution being ascertained by the Klobbie method[7]. The osmium content of the test solutions was 49.12 μg Os/ml and 41.44 μg Os/ml, respectively.

The following reagents were used: I, The amide of α-thiosemicarbazido-isobutyric acid[8]; II, α-thiosemicarbazido-isobutyronitrile[8]; III, 3,5-dihydroxy-6-mercapto-1,2,4-triazine (disodium salt)[9]; IV, 3-mercapto-5-hydroxy-6-methyl-1,2,4-triazine[10]; V, 3-mercapto-5-hydroxy-6,6-dimethyl-1,6-dihydro-1,2,4-triazine[8]; VI, 2-mercapto-4-hydroxy-6-methyl-1,3-pyrimidine[11].



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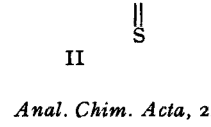

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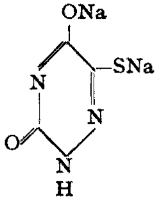

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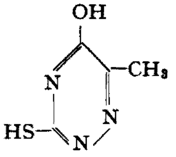

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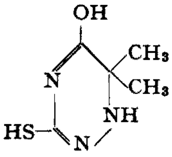

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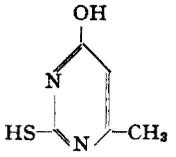

VI

Reagents I and II were used as 0.1% solutions in 1% sodium hydroxide. Reagent III was used as a 0.2% solution in water. Reagents IV, V and VI were used as 0.2% solutions in 1% sodium hydroxide. In each case 2 ml of reagent solution was added both to the test solution and to the blank.

Procedure

Pipette 0.25–6 ml of the osmium solutions in to 10-ml calibrated beakers. With reagents I, II, III, IV and VI, add 1 ml of sulphuric acid solution (32 ml of concentrated acid and 68 ml of water), while with reagent V, add 0.25 ml of the same acid solution. Then add the reagent solution and dilute to 10 ml with ethanol. With reagent I, a yellow colour is obtained which develops steadily, the reading being taken after 10 min. With reagent II, a yellow-brown colour is obtained, the reading being taken during the first 5 min. With reagent III, a red-brown colour is obtained, the reading being taken during the first 10 min since the extinction decreases steadily. With reagent IV, a yellow colour is obtained which develops steadily, the reading being taken after 20 min. With reagent V, a yellow colour is obtained, the reading being taken during the first 10 min since the extinction decreases steadily. With reagent VI, a pink shade is obtained.

Owing to the fact that reagent VI exhibits a low sensitivity, quantitative tests were carried out with the first five reagents only.

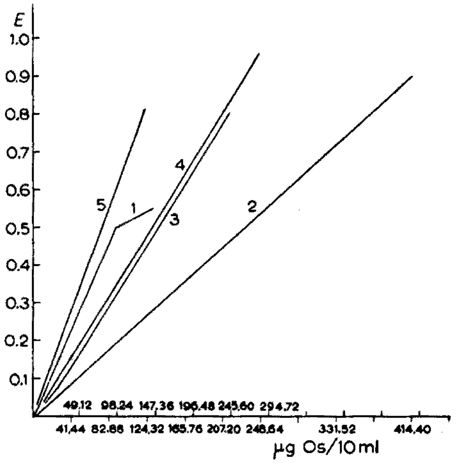

Fig. 1. Extinction curves. 1. I M-43; 2. II M-43; 3. III M-47; 4. IV M-50; 5. V M-43.

TABLE I

ml Os solution	*µg Os per 10 ml*	*Reagent I M-43*	*Reagent II M-43*	*Reagent III M-47*	*Reagent IV M-50*	*Reagent V M-43*	*Reagent VI M-43*
0.25	12.28	0.06	—	0.04	—	—	—
	10.36	—	—	—	0.04	0.07	—
0.5	24.56	0.125	—	0.08	—	—	—
	20.72	—	0.045	—	0.08	0.145	—
1.0	49.12	0.25	—	0.16	—	—	—
	41.44	—	0.09	—	0.16	0.29	—
2.0	98.24	0.50	—	0.32	—	—	—
	82.88	—	0.18	—	0.32	0.58	0.08
3.0	147.36	0.55	—	0.48	—	—	—
	124.32	—	0.27	—	0.48	0.81	—
4.0	196.48	—	—	0.64	—	—	—
	165.76	—	0.36	—	0.64	—	—
5.0	245.60	—	—	0.80	—	—	—
	207.20	—	0.45	—	0.80	—	—
6.0	294.72	—	—	—	—	—	—
	248.64	—	0.54	—	0.96	—	—
higher concentration	331.52	—	0.72	—	—	—	—
higher concentration	414.40	—	0.90	—	—	—	—

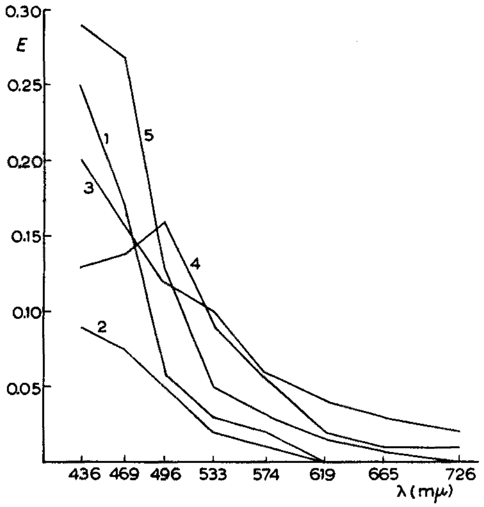

Fig. 2. Colour curves. 1. I-49.12 µg Os/10 ml; 2. II-41.44 µg Os/10 ml; 3. III-49.12 µg Os/10 ml; 4. IV-41.44 µg Os/10 ml; 5. V-41.44 µg Os/10 ml.

Readings were taken by means of a vertical Pulfrich photometer, the maximum extinction being obtained on the M-43 filters with reagents I, II, III, V and VI, and on the M-50 filter with reagent IV. The results are shown in Table I and in Figs. 1 and 2.

The results shown in Table I and Fig. 1 show that reagent I allows the determination of osmium in the range 1.23–9.82 μg Os/ml; reagent II, in the range 2.07–41.44 μg Os/ml; reagent III, in the range 1.23–24.56 μg Os/ml; reagent IV, in the range 1.04–24.86 μg Os/ml; reagent V, in the range 1.04–8.29 μg Os/ml.

These results, as well as the data mentioned in a recent paper[6], show that both from sensitivity and colour stability considerations, the reagents derived from thiourea are to be preferred to those containing a heterocyclic nucleus with the —SH group attached to the ring.

SUMMARY

The reaction of osmium is examined with two thiourea derivatives and four heterocyclic nitrogen compounds containing the SH-group attached to the ring, and five new colorimetric methods for the determination of osmium in the range 1.04–41.44 μg Os/ml are proposed.

RÉSUMÉ

Après avoir examiné le comportement de l'osmium avec deux dérivés de la thiourée et quatre composés hétérocycliques azotés renfermant un groupe SH, les auteurs proposent cinq nouvelles méthodes pour le dosage colorimétrique de cet élément.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Reaktion von Osmium mit Derivaten des Thioharnstoffs und mit N-heterocyclen, die eine SH-Gruppe tragen. Es werden 5 neue colorimetrische Bestimmungsmethoden für Osmium vorgeschlagen.

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THIONIN DERIVATIVES IN THE EXTRACTION AND DIRECT PHOTOMETRIC DETERMINATION OF BORON*

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Monomethylthionin and methylene blue (tetramethylthionin) have been thoroughly investigated by PÁSZTOR *et al.*[1,2] and DUCRET[3] and applied to the extraction and direct determination of boron. A detailed investigation has shown that other commercially available thionin derivatives can also be used advantageously for the same purpose. Thionin itself is not satisfactory but dimethylthionin (Azure A), trimethylthionin (Azure B), dimethyl-diethylthionin (New Methylene Blue N), mono-nitro-tetramethylthionin (Methylene Green), methyl-N-dimethylthionin (Toluidine Blue O) and the eosinates of Azure A and B were found suitable. In addition more than thirty solvents, mostly chlorinated or brominated hydrocarbons, were tried as extraction media. Using different dyes and solvent combinations various boron concentration ranges can be covered with good accuracy and reproducibility.

APPARATUS AND REAGENTS

Apparatus

For the spectrophotometric work a Beckman Model DU and a Cary recording spectrophotometer were used with 1-cm quartz cells. For the routine part of this work the Model B Beckman spectrophotometer was used. Except for storing and measuring the organic solvents polyethylene ware was used in all experimental work.

Reagents

Standard borofluoride (BF_4^-) solution containing 1.0 μg of boron per ml was prepared by dissolving reagent grade boric acid in 0.25% HF. This solution was used only after standing 24 h to insure complete formation of BF_4^-. 0.001-*M* aqueous dye solutions were prepared from commercially available (National Aniline) dyes. Reagent grade organic solvents were used for the extractions. Mixed solvents were prepared just before the extraction was carried out.

All reagents except the organic solvents were kept in polyethylene bottles and those containing hydrofluoric acid were kept below 5°. (No purification of reagents was carried out unless noted.)

PROCEDURE

10.0 ml of standard BF_4^- solution (containing 10 μg B) were diluted in a 100-ml polyethylene bottle with 30.0 ml of water or 0.5 *N* H_2SO_4. 10.0 ml of 0.001 *M* dye

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* This paper was presented at the 1960 fall meeting of the American Chemical Society in New York.
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solution and then 25.0 ml of the organic solvent were added. The bottle was capped and shaken well for at least 1 min. After the layers separated completely the absorbance characteristics of the organic phase were investigated and subsequent quantitative measurements made at the absorbance maximum. Reagent blanks were run in parallel.

If the absorbance was too high the organic phase was diluted (1 : 5 or 1 : 25) with the solvent so that the final absorbance was always less than 1.2. Reagent blanks were treated the same way and their values subtracted from the total absorbance to give the net absorbance.

DISCUSSION

The structure of methylene blue, first used for the solvent extraction of boron by Ducret[3], suggested that other thionin derivatives or thionin itself might also be applicable. The commercially available derivatives, therefore, were investigated.

Preliminary experiments, using dichloroethane, carried out as described in the procedure, showed visually that most of the dyes form an extractible complex with BF_4^-. These were, in decreasing order of visible difference, MB (Methylene Blue), AB (Azure B), NMB (New Methylene Blue N), AB-eos. (Azure B Eosinate), AA-eos. (Azure A Eosinate), MG (Methylene Green), AC (Azure C), AA (Azure A), and TBO (Toluidine Blue O). No visible difference was observed with T (Thionin). The structural formulas of these dyes can be seen in Fig. 1.

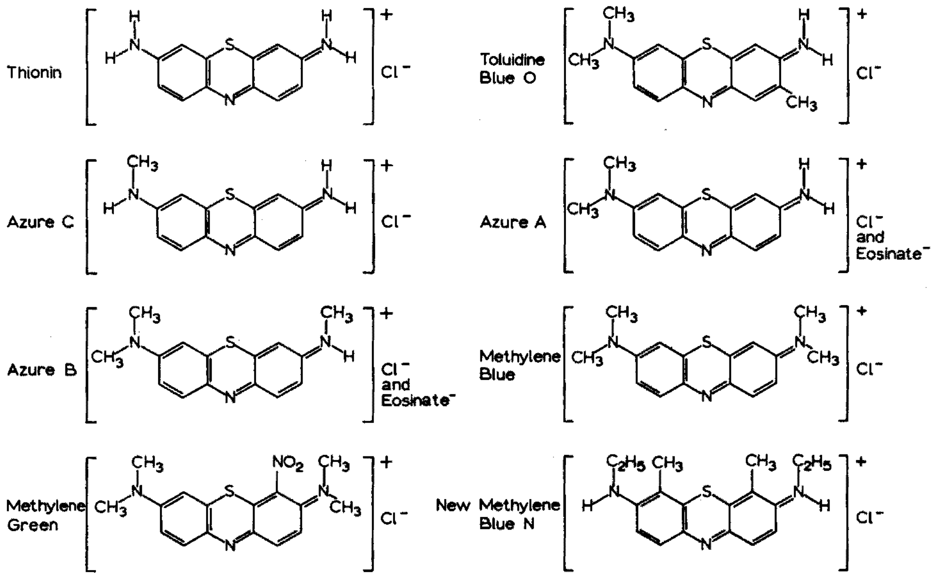

Fig. 1. Thionin derivatives tested.

Spectrophotometric measurements were carried out on solutions obtained by using the general procedure. It was observed that where a BF_4^-–dye complex was formed and extracted (with the exception of TBO and NMB), the absorbance maximum was between 655–660 mμ (that of TBO was at 632 mμ and of NMB at 618 mμ) (Fig. 2). The absorbance maximums of the reagent blanks were approximately at the same wave lengths as their corresponding BF$_4^-$–dye complexes with the exception of TBO. These anomalous curves of TBO are shown in Fig. 2.

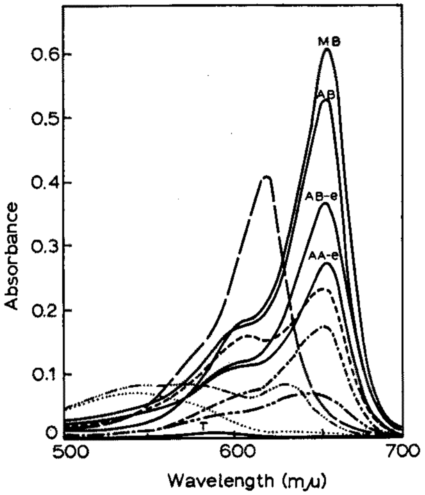

Fig. 2. Spectral absorbance curves of the extracted BF$_3$–dye complexes: ———— MB, AB, AB-e, AA-e, T; —— —— NMB; — — — — MG; - — - — - — AC; - - — - - - — AA; ···—···— TBO; .... TBO reagent blank.

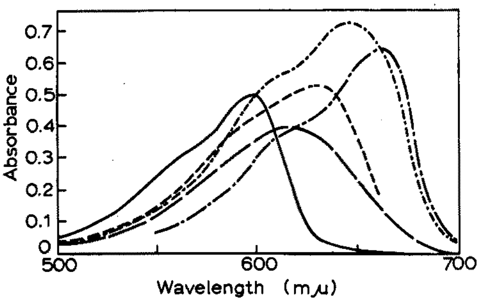

Fig. 3A. Spectral absorbance curves of 10^{-5} *M* aqueous dye solutions at pH = 3.0: ———— Thionin; —— —— —— Azure C; — — — — — Azure A; - — - — - — - — Azure B; - —— - —— Methylene Blue.

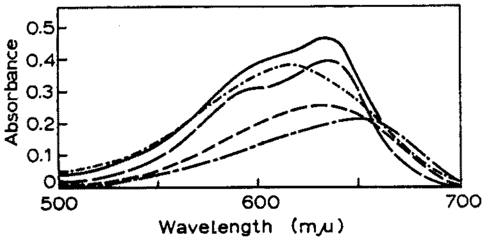

Fig. 3B. ———— Toluidine Blue O; —— —— —— New Methylene Blue; — — — — — Azure A-eosinate; —— - —— - —— - Azure B-eosinate; - — - — - — - — Methylene Green.

The absorbance maxima of these dyes in the original aqueous solutions varied from 614–663 mμ except for T at 597 mμ (Figs. 3 A and B).

Measurements with T showed a highest total absorbance value of less than 0.02 and a net absorbance less than 0.01 for 10 μg B. Net absorbances using the other dyes, again for 10 μg B, were of the following order (those greater than 1.2 are extrapolated values). MB 2.9, AB 2.0, NMB 1.9, AB-eos 1.6, AA-eos and MG 1.2, AC 1.0, AA and TBO 0.4. The reagent blank absorbance values decreased in the same order from 0.6 for MB to 0.08 for TBO. These results showed that by using different dyes with the same solvent (1,2-dichloroethane) various boron concentration ranges could be covered with good sensitivity without aliquoting, making most of the dyes attractive for analytical applications.

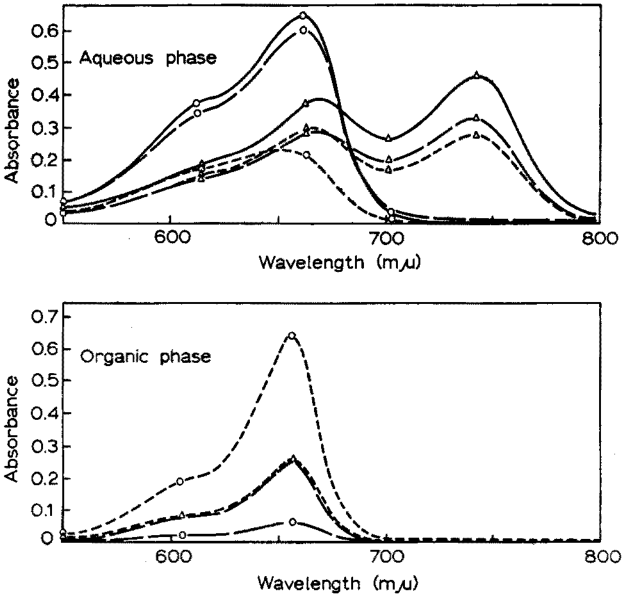

Fig. 4. Effect of pH and dichloroethane extraction on the absorbance curves of 10^{-5} *M* methylene blue solution. pH = 2.0: o———o before extraction; o— —o extracted–blank; o - - - - o extracted–10 μg B(as BF_4^-). pH = 0.0: Δ———Δ before extraction; Δ— —Δ extracted–blank; Δ- - - - -Δ extracted–10 μg B(as BF_4^-).

Figs. 4 and 5 show the effect of pH and extraction on both the aqueous and organic phases for Methylene Blue and Azure C with dichloroethane. The total and net absorbances do not change between pH 6 and 2 but decrease at lower pH levels[1,2]. The same trend was observed with other dyes. Correct results can be obtained between pH 2 and 0.25 by using higher dye concentrations and carefully controlling the acid concentration

To further improve the solvent extraction of boron with these thionin derivatives, various organic solvents were tried. Different solvent types were first checked including halogenated hydrocarbons, benzene, ethers and carbon disulfide. The BF_4^-–dye complexes behaved quite differently with the various solvents. Some did not extract the complex at all but others, especially several of the chlorinated hydrocarbons (and to a lesser extent a brominated hydrocarbon) were universally suitable. Also the distribution of the colored boron complex between the aqueous and organic layers varied significantly.

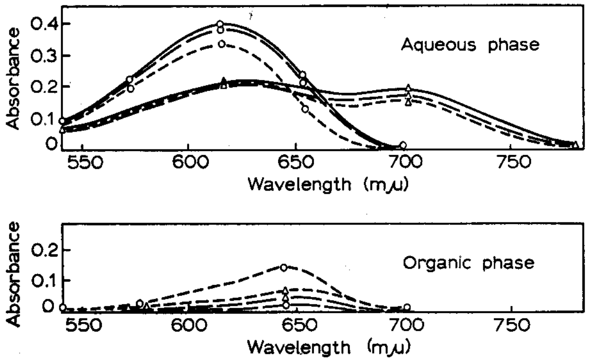

Fig. 5. Effect of pH and dichloroethane extraction on the absorbance curve of 10^{-5} M monomethyl thionin solution. pH = 2.0: o———o Before extraction; o—— ——o extracted–blank; o— — — —o extracted–10 μg B(as BF_4^-). pH = 0.0: Δ———Δ before extraction; Δ—— ——Δ extracted–blank; Δ— — — —Δ extracted–10 μg B (as BF_4^-).

No, or very limited, extraction was observed with benzene, 1,3-dimethylbenzene, diethylether, methylethylether, carbon disulfide, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, 2-chloropropane, 1-chlorobutane, chlorobenzene, *p*-dichlorobenzene in benzene, tetrachlorobenzene in benzene, hexachlorobenzene in benzene, hexachloroethane in benzene, bromoethane, 1,1,2,2,-tetrabromoethane and 1,2-dibromopropane. With all these solvents the total absorbance was less than 0.04 and the net absorbance less than 0.02 for 10 μg boron.

Carbon tetrachloride, chloroform and monochloroethane were found to be poor extracting solvents, the highest net absorbance values, those for MB, being respectively 0.02, 0.07 and 0.07. Monochloroethane, with a low boiling point, is also disadvantageous because the extraction must be carried out at around 6° or less.

Dichloromethane and *cis*-dichloroethylene behave similarly to 1,2-dichloroethane in that they give the highest net absorbances. Unfortunately the reagent blanks are relatively high for MB, AB, and NMB and 10 μg boron can be measured only after 1 : 5 dilution. With AB-eosinate, MG, AC, AA-eosinate, AA, and TBO, lower reagent blanks and satisfactory net absorbance values were obtained.

1,1,2-Trichloroethane and *o*-dichlorobenzene give lower absorbance values with correspondingly lower reagent blanks. *o*-Dichlorobenzene gives exceptionally low blanks with MB, and AB, making it an especially good solvent for use with these dyes. 1,2-Dichloropropane and 1,4-dichlorobutane extract the boron complexes even less but can be used for higher boron concentrations.

The dyes themselves are relatively soluble in 1,1,2,2,-tetrachloroethane and di-(β-chloroethyl)-ether making a 1 : 5 or 1 : 25 dilution of the extract necessary in order to read the absorbance. Although even with a 1 : 25 dilution measurable net absorbances were obtained, the high reagent blanks (80–95% of the total absorbance) make these solvents unsatisfactory. These were the only solvents that extracted the T–BF_4^--complex appreciably, giving net absorbances of 0.25 and 0.36.

The brominated solvents with the exception of 1,2-dibromethane, which was a very poor extractant, proved completely unusable.

Solvent mixtures were also tried. Mixing a solvent into which the colored BF_4^--complex extracts readily with one which is a poor extractant makes adjustment of the sensitivity and range possible. An example of this is the use of 1,2-dichloroethane-1,2-dichloropropane (or carbon tetrachloride) mixtures with monomethylthionin as previously reported[2]. Many other variations are obviously possible.

The measurements reported in this paper were carried out according to the procedure using water as the diluent for the aqueous phase. When diluted sulfuric acid was used instead of the water, the same trends were observed but the net absorbance decreased with increasing acid concentrations[1,2]. Organic acids as well as nitric and, in higher concentrations, hydrochloric and hydrofluoric acids interfere.

Total and net absorbances depend not only on pH but also on the purity of the dye and of the solvent. Generally it can be stated that if the aqueous dye solution was purified by preliminary extraction with the solvent, reagent blanks were lowered by about 10%.

Organic acid impurities in the solvent will also cause high blank values and erroneous results. Extracting with 1 *N* aqueous NaOH and redistilling the solvent will eliminate these impurities. The commercial solvents used in our work did not contain enough impurities to warrant purification.

CONCLUSIONS

Thionin and nine of its derivatives form complexes with BF_4^- and, except for that of thionin itself, these can be used for solvent extraction and photometric determina-

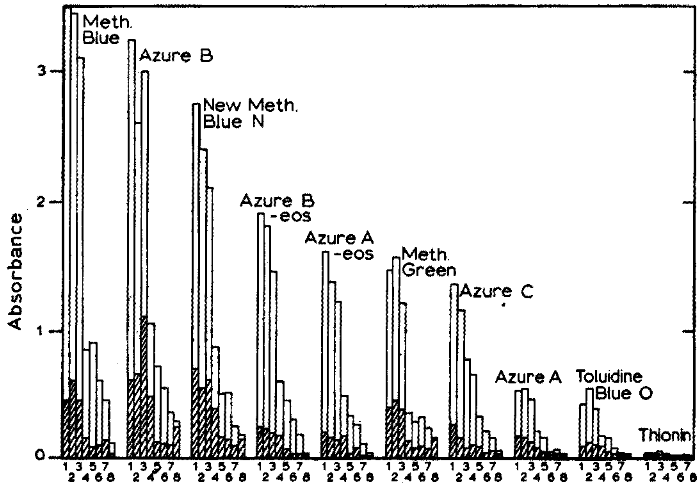

Fig. 6. Extractability of BF_3–thionin derivative complexes into different solvents. 1. *cis*-dichloroethylene; 2. 1,2-dichloroethane; 3. dichloromethane; 4. 1,1,2-trichloroethane; 5. *o*-dichlorobenzene; 6. 1,4-dichlorobutane; 7. 1,2-dichloropropane; 8. trichloromethane; ☐ net absorbance; ▨ blank.

tion of boron. The complexes of the various dyes are extractible to different extents, but generally in the same order, in different solvents (Fig. 6) and solvent mixtures.

For analytical applications the following combinations can be recommended:

Dichloromethane 1,2-dichloroethane *cis*-dichloroethylene	AC, AA, AA-eos., TBO.
o-dichlorobenzene 1,1,2-trichloroethane	AC, AA-eos., AB, AB-eos., MB.
1,2-dichloropropane 1,4-dichlorobutane	AB and MB.

With solvent mixtures many other useful combinations are possible with all the thionin derivatives discussed here.

SUMMARY

Thionin and nine commercially available thionin derivatives were studied for their applicability in the analytical solvent extraction and direct photometric determination of boron. Azure A, Azure B, Azure C, Methylene Blue, New Methylene Blue N, Methylene Green, Toluidine Blue O, Thionin and the eosinates of Azure A and B were investigated. Over thirty organic solvents, mostly chlorinated or brominated were tried with these dyes. 1,2-Dichloroethane, 1,2-dichloropropane, dichloromethane, 1,1,2-trichloroethane, *cis*-dichloroethylene, *o*-dichlorobenzene, 1,4-dichlorobutane and mixtures of these solvents proved applicable. Many good dye–solvent combinations were found which were very attractive for the separation and determination of various amounts of boron. Only thionin itself proved unsatisfactory.

RÉSUMÉ

La thionine et neuf de ses dérivés ont été examinés en vue de leur utilisation pour l'extraction et le dosage photométrique du bore. Plusieurs solvants organiques ont été essayés. Seule la thionine n'a pas donné de résultats satisfaisants.

ZUSAMMENFASSUNG

Thionin und neun Derivate des Thionins wurden auf ihre Eignung zur photometrischen Bestimmung von Bor untersucht. Die zur Extraktion verwendbaren organischen Lösungsmittel werden angegeben. Thionin selbst ist nicht geeignet für die Bestimmung.

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DETERMINATION OF SULPHANILAMIDES WITH ALKYL NITRITES BY A POTENTIOMETRIC METHOD

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In the field of organic functional group analysis sulphanilamides have attracted special attention owing to their pharmaceutical importance. Several of the methods reported for the determination of sulphanilamides are based on acidimetric titrations of the amino group present in the molecule. Owing to the weak basic character of the amino group, the application of a non-aqueous titration and potentiometric end-point detection is necessary[1]. FRITZ AND KEEN[2] attempted the titration of the very weak acidic group $-SO_2NH-$ in non-aqueous media such as butylamine or dimethylformamide.

Certain recommended methods for aminosulphonamides depend on reactions of the amino group and such methods are mainly satisfactory. In general, acidimetric titrations are not specific for the sulphanilamides and hence reactions such as diazotisation[3] have been found more satisfactory (the method has been recognised as an official method)[4]; several workers have employed a diazotisation procedure with sodium nitrite as titrant and starch-iodide paper as external indicator or acriflavine[5] or diphenylbenzidine violet[6] as internal indicator; potentiometric end-point detection has also been applied.

Because of the limitations of sodium nitrite for quantitative diazotisation, MATHUR *et al.*[7] have recently employed alkyl nitrites for the determination of certain aromatic primary amines and compounds containing a reactive methylene group. Since alkyl nitrites were found to have advantages over sodium nitrite for quantitative diazotisation, the method has been extended to the determination of sulphanilamides.

EXPERIMENTAL

The procedure adopted for the preparation and standardisation of the alkyl nitrite solution was the same as described earlier[7]. Twice recrystallised sulphanilamide was used as primary standard as recommended by CALAMARI *et al.*[3]. The standard butyl nitrite solution was used to determine the amount of certain sulpha drugs in the commercial preparations. The titration was performed potentiometrically with a S.C.E. *vs.* a bright platinum indicator electrode, the equivalence point being indicated by a sudden change in the potential of the order of 80–120 mV. The sulpha drugs (tablets) employed in the present investigation were Sulphadiazine (Lederle), Sulphathiazole (Ciba), Sulphaguanidine (Ciba), Sulphapyridine (I.C.I.), Sulphamethazine (Ciba) and Sulphamerazine (Ciba). The graph (Fig. 1) represents a typical potentiometric titration curve of sulphadiazine and butyl nitrite. The sulpha drug contents of the tablets given by the manufacturer and the values found experimentally are shown in the Table I.

In addition to the classical method, the "dead stop" technique with two platinum electrodes and a very small E (approximately 15 mV) was also used for end-point detection. The end-point is indicated by a sudden increase in the current due to depolarisation of the electrodes when a slight excess of nitrous acid is present.

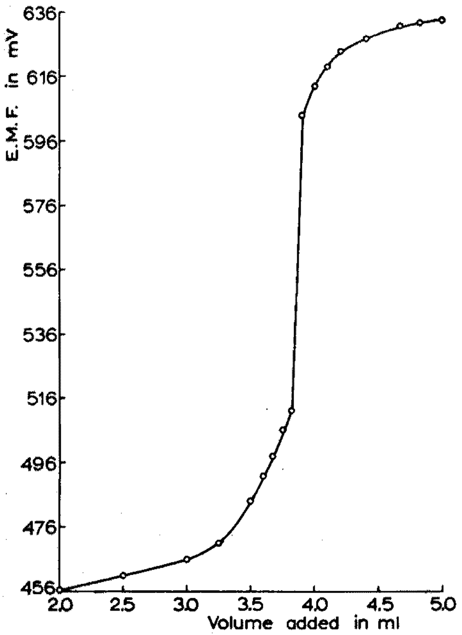

Fig. 1. Titration curve of sulphadiazine and butyl nitrite.

TABLE 1

Name of the sulpha drug	*Amount of sulpha drug per tablet*	
	Manufacturer's specification (g)	*Found (g)*
Sulphadiazine	0.5	0.487
Sulphathiazole	0.5	0.502
Sulphaguanidine	0.5	0.479
Sulphapyridine	0.5	0.484
Sulphamethazine	0.5	0.491
Sulphamerazine	0.5	0.478

ACKNOWLEDGEMENT

The authors are very grateful to PROF. K. P. HALDAR for his keen interest.

SUMMARY

A potentiometric titration with alkyl nitrite solutions is described for the determination of various sulpha drugs.

RÉSUMÉ

Une méthode est proposée pour le dosage potentiométrique de dérivés sulfamidés, au moyen de nitrite d'alcoyle.

ZUSAMMENFASSUNG

Beschreibung einer potentiometrischen Methode zur Bestimmung von Sulfamiden mit Hilfe von Alkylnitrit.

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OSZILLOPOLAROGRAPHISCHER NACHWEIS UND BESTIMMUNG VON JODAT UND PERJODAT

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In letzter Zeit untersuchten wir die Möglichkeit eines einfachen und schnellen Nachweises[1] und der Bestimmung[2] von Jodat neben Perjodat und umgekehrt. Dieses Problem ist wichtig nicht nur in der industriellen Praxis, wie z.B. bei der Erzeugung von Perjodsäure und bei der Reinheitskontrolle der bereiteten Präparate, sondern auch bei der Untersuchung der Oxydation von organischen Stoffen mit Perjodsäure und ihren Salzen.

Bei der oszillographischen Untersuchung (Verfolgung der Kurven $dV/dt = f(V)$) der angeführten Stoffe hat es sich gezeigt, dass es mit der oszillographischen Methode möglich sein wird nicht nur einen verlässlichen Nachweis durchzuführen, sondern auch beide Stoffe mikroquantitativ zu bestimmen. In der vorgelegten Arbeit wurde ausserdem eine Methode ausgearbeitet, die die Bestimmung auch von sehr kleinen Mengen Jodat in Perjodat und Perjodat in Jodat möglich macht.

EXPERIMENTELLER TEIL

Reagenzien

Kaliumjodat, Kaliumperjodat (KIO_4), Kaliumchlorid, Kaliumnitrat, Kaliumphosphat, Natriumperchlorat, Natriumazetat, Natriumsulfat, Kaliumkarbonat, Kaliumbikarbonat, Kaliumhydroxyd, Natriumhydroxyd, Chlorwasserstoffsäure, Schwefelsäure, Phosphorsäure, Oxalsäure, Essigsäure (p.a. Merck und Lachema). $(NH_4)_2H_3IO_6$, $K_4I_2O_9 \cdot 9\ H_2O$ und $NaIO_4 \cdot 3\ H_2O$ wurden laboratoriumsmässig hergestellt*.

Apparatur

Zur Verfolgung der Kurven der Funktion $dV/dt = f(V)$ wurden Elektronenröhren-Polaroskope Křižík P524 und P576 verwendet. Die Dauer des Quecksilbertropfens wurde mit einem mechanischem Tropfenabtrenner konstant gehalten.

Die Kurven wurden mit einem Fotoapparat Praktina aufgenommen, mit einem Flexon Objektiv mit Blende 1:2, mit Zwischenring, aus einer Entfernung von 25 cm auf Agfa Rapid Film. Die Expositionszeit war 1/25 oder 1/10 sec.

Als Vergleichselektrode wurde eine gesättigte Kalomelelektrode, der Quecksilberboden oder eine Graphitelektrode angewandt. Entsprechend der Konzentration der Ionen in der analysierten Lösung muss die Grösse des aufgezwungenen Stromes

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* Wir danken Dr. M. DRÁTOVSKÝ vom Lehrstuhl für anorganische Chemie der Karlsuniversität in Prag, der uns diese Verbindungen zur Verfügung gestellt hat.

gewählt werden. Sie soll "so klein als möglich" sein, damit keine Störungen an der Quecksilbertropfelektrode entstehen.

ERGEBNISSE

Das oszillographische Verhalten von Jodat und Perjodat

Während in sauerem Medium (1 M HCl, 1 M H_2SO_4, 1 M H_3PO_4, 1 M Essigsäure und 1 M Oxalsäure) keine geeigneten Bedingungen für das Unterscheiden der beiden untersuchten Verbindungen gefunden wurden, wurde in neutralem, schwach alkalischem und alkalischem Medium gefunden, dass die Depolarisation von Perjodat und Jodat bei der Verfolgung der Kurven $dV/dt = f(V)$ sich durch klar ausgeprägte Einschnitte bemerkbar macht. In 1 M Lösungen von Natriumperchlorat, Natriumsulfat, Kaliumchlorid, Kaliumnitrat, Kaliumphosphat und Natriumazetat bildet Perjodat in dem kathodischen Teil der Kurve zwei Einschnitte, von denen der mehr positiv gelegene ($E = -0.1$ V S.C.E.) der Reduktion von Perjodat zu Jodat entspricht, und der zweite, der bei negativen Potenzialen auftritt ($E = -1.4$ V S.C.E.) der Reduktion von Jodat zu Jodid (Fig. 1). Die Reduktion von Jodat macht sich nur durch einen einzigen Einschnitt bemerkbar, dessen Depolarisationspotenzial ($E = -1.4$ V) dasselbe ist wie bei dem zweitem, mehr negativem Einschnitt des Perjodats; das wurde durch die Vertiefung und Vergrösserung dieses Einschnittes nach Zugabe von Jodat zu einer Perjodatlösung bewiesen. Um sicher zu sein, dass der kleinere, mehr positiv gelegene Einschnitt des Perjodats nicht durch eine eventuelle Verunreinigung des verwendeten Präparates verursacht wird, wurden dieselben Messungen auch mit Lösungen von $(NH_4)_2H_3IO_6$, $K_4I_2O_9 \cdot 9\ H_2O$ und $NaIO_4 \cdot 3\ H_2O$, die laboratoriumsmässig bereitet wurden, durchgeführt.

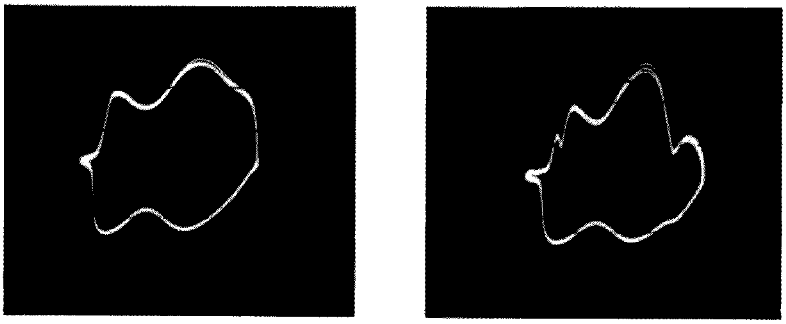

Fig. 1. Oszillogramme von Perjodat. (a) 5 ml 1 M KNO_3; (b) 5 ml 1 M KNO_3 + 0.15 ml 0.01 M KIO_4.

Da bekannt ist, dass die Redoxpotentiale beider Systeme durch den pH-Wert beeinflusst werden[3], wurde im weiteren das oszillographische Verhalten beider Verbindungen im Medium von Karbonatpuffern und alkalischen Hydroxyden untersucht.

In Lösungen von Karbonatpuffern von pH 8.4 bis 11.08 macht sich die Reduktion von Perjodat und Jodat auf diesselbe Weise bemerkbar, wie im Medium von neutralen Elektrolyten. Auf diese Weise ist es also nur möglich, Perjodat neben Jodat nachzuweisen. In allen Fällen ist es möglich, in 5 ml Elektrolyt 0.1 mg KIO_4 in Gegenwart von grossen Jodatkonzentrationen nachzuweisen (Wechselstromkomponente: 0.2–0.6 mA — entsprechend der Jodatkonzentration — Empfindlichkeit 3–5, Quecksilbertropfelektrode-Bodenquecksilber).

In Kaliumhydroxydlösungen werden mit wachsender Konzentration im Bereich 0.2–5 *M* KOH beide Perjodateinschnitte weniger deutlich. Bei Hydroxydkonzentrationen höher als 2.5 *M* verschwindet praktisch der mehr negativ gelegene Einschnitt ($E = -1.4$ V), wobei an dem kathodischen Teile der Kurve bei mehr negativen Potentialen eine Deformation in Form einer länglichen Ausbuchtung auftritt. Das Jodat bildet aber unter denselben Bedingungen im ganzen untersuchten Konzentrationsbereich des Hydroxyds einen scharfen, ausgeprägten Einschnitt, dessen Potential sich praktisch nicht ändert ($E = -1.4$ V). Das kann zum Nachweis von Jodat neben Perjodat ausgenützt werden. In 5 ml 5 *M* KOH kann 0.1 mg KIO_3 verlässlich nachgewiesen werden. Bei Verwendung von Natriumhydroxyd als Elektrolyt (0.2–5 *M* NaOH) wurden praktisch dieselben Ergebnisse erzielt. Bei höheren Perjodatkonzentrationen entsteht zwar ein Niederschlag von Natriumperjodat, wodurch aber der Nachweis von Jodat nicht in grösserem Ausmasse beeinflusst wird.

Nachweis und Bestimmung von Perjodat in Jodat

Zum Nachweis und zur Bestimmung von Perjodat in Jodat kann als Elektrolyt direkt die wässerige Lösung der zu analysierenden Probe angewandt werden. Die Anwesenheit von Perjodat macht sich durch einen scharfen Einschnitt am kathodischen Teil der Kurve kenntlich, ($E = -0.1$ V S.C.E.), der derselbe ist wie der erste Einschnitt in anderen Lösungen neutraler Elektrolyte (Fig. 2).

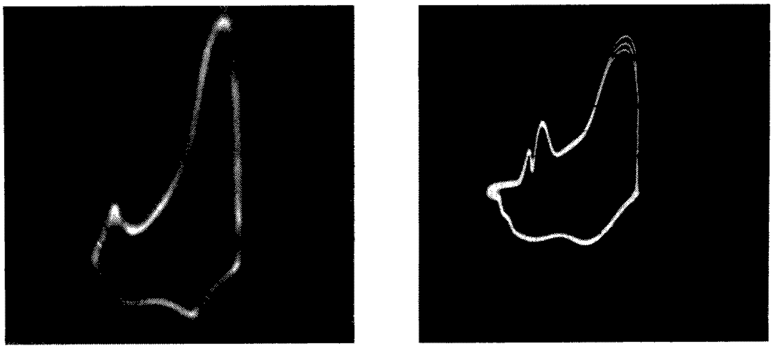

Fig. 2. Nachweis von Perjodat in Jodat. (a) 0.4 g KIO_3 in 5 ml H_2O; (b) 0.4 g KIO_3 + 0.46 mg KIO_4 in 5 ml H_2O.

Arbeitsgang. Eine Einwaage von 0.8 g KIO_3 wird in einem Messkolben von 10 ml Volumen in destilliertem Wasser gelöst und aufgefüllt. Nach volkommenem Durchmischen werden 5 ml in das elektrolytische Gefäss abpipettiert, und nach Einschalten des Gerätes wird die quantitative Auswertung entweder mittels der Methode der verschiebbaren Lichtachse, oder mittels der Methode der oszillographischen Komparationstitration[4] vorgenommen.

Aus dem Diagramm der Abhängigkeit der Einschnittiefe von der Perjodatkonzentration (Fig. 3) geht hervor, dass optimale Ergebnisse unter den gegebenen Bedingungen dann erzielt werden, wenn die Konzentration des Perjodats im Jodat im Bereich von 0.05–0.17% liegt, d.h. dass eine Probe die mit einer höheren Perjodatkonzentration verunreinigt ist bei der Bereitung der Lösung mehr verdünnt werden muss, oder dass mit einer kleineren Einwaage gearbeitet werden muss.

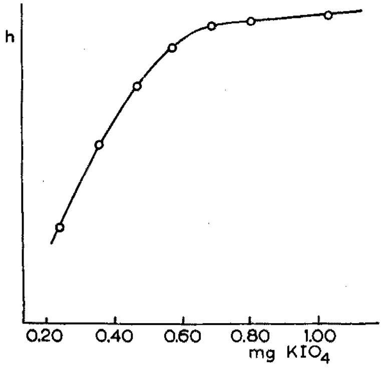

Fig. 3. Abhängigkeit der Tiefe des kathodischen Einschnitts des Perjodats von der Konzentration des KIO_4 in KIO_3 (0.4 g KIO_3 in 5 ml H_2O).

Der Fehler der Bestimmung bei Anwendung der Methode der verschiebbaren Achse, unter den angegebenen Bedingungen überschreitet nicht ± 10% des Ergebnisses. Bei Anwendung der Methode der Komparationstitration wird als Vergleichselektrolyt ein reines Jodatpräparat, frei von Perjodatspuren, verwendet: in diesem Falle überschreitet der Fehler der Bestimmung nicht ± 5% des Ergebnisses.

Nachweis und Bestimmung von Jodat in Perjodat

Für den Nachweis und die Bestimmung von Jodat in Perjodat wurde als der geeignetste Grundelektrolyt eine 5 *M* Natriumhydroxydlösung verwendet, in der Perjodat nur wenig löslich ist. Bei der Verwendung von Kaliumhydroxyd deformiert die hohe Perjodatkonzentration in der Lösung stark die Kurve der verfolgten Funktion. Der Potentialbereich ist dabei stark beschränkt, und auch bei Anwendung der höchsten Wechselstromstärken macht sich eine kleine Jodatkonzentration nicht durch einen Einschnitt bemerkbar. Kaliumhydroxyd wurde also nur zur Lösung der zu analysierenden Proben benutzt, durch Zugabe von Natriumhydroxyd wurde die Perjodatkonzentration durch Bildung eines Niederschlages so weit herabgesetzt, das der Jodateinschnitt gut kenntlich wurde und zu der Bestimmung verwendet werden konnte.

Arbeitsgang. Eine Einwaage von 1 g Kaliumperjodat wird in einem 10 ml Messkolben in 5 ml 5 *M* KOH gelöst, und nach volkommenem Durchmischen wird die Lösung schnell mit 10 *M* NaOH aufgefüllt. Nachdem wieder durchgemischt wurde, lässt man den Niederschlag absetzen, 5 ml der Lösung werden in das elektrolytische Gefäss genau abgemessen und nach Einschalten des Gerätes wird die quantitative Auswertung entweder mittels der Methode der verschiebbaren Lichtachse oder mittels der

Methode der oszillographischen Titration vorgenommen. Optimale Ergebnisse werden dann erzielt, wenn die Konzentration von Jodat im Perjodat im Bereich von 0.2–1% liegt.

Der Fehler der Bestimmung ist in diesem Falle etwas grösser, ±10–20% des Ergebnisses, denn der Jodateinschnitt wird durch eine hohe Perjodatkonzentration in der Lösung in gewissem Ausmasse beeinflusst (Fig. 4) und seine Messung ist schwieriger als im Falle der Bestimmung von Perjodat in Jodat.

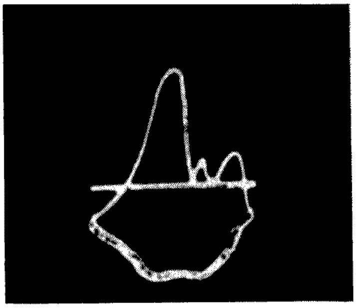

Fig. 4. Bestimmung des Jodats in Perjodat (0.8% KIO_3 in KIO_4).

ZUSAMMENFASSUNG

Es wurde das oszillopolarographische Verhalten von Perjodat und Jodat in saueren, neutralen und alkalischen Elektrolyten untersucht. Der Nachweis und die Bestimmung von Perjodat in Jodat kann unter Verwendung von Jodat als Elektrolyt vorgenommen werden, der Nachweis und die Bestimmung von Jodat in Perjodat unter Verwendung von 5 *M* Natriumhydroxyd als Elektrolyt.

SUMMARY

The oscillopolarographic behaviour of periodate and iodate has been investigated in acid, neutral and alkaline electrolytes. The detection and determination of periodate in iodate may be carried out using iodate as electrolyte and the detection and determination of iodate in periodate may be carried out using 5 *M* sodium hydroxide as electrolyte.

RÉSUMÉ

Les auteurs ont effectué une étude sur le comportement oscillopolarographique des periodate et iodate, dans divers milieux. Ils proposent des méthodes de dosage et d'identification pour ces deux anions, l'un en présence de l'autre.

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THE USE OF MICROCHEMICAL METHODS IN RADIOCHEMICAL ANALYSIS

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INTRODUCTION

The radiochemical analysis of a mixture of radioactive materials such as fission products normally involves the following essential series of operations:

(*a*) Addition to the sample of known amounts of carriers for the radioactive nuclides to be determined.

(*b*) Appropriate chemical treatment to ensure complete interchange between the inactive and active species.

(*c*) Chemical separation of the required elements from each other and any inactive materials present in the mixture.

(*d*) Rigorous radiochemical purification of each separated element to remove all traces of active impurities.

(*e*) Determination of the chemical yield of each carrier.

(*f*) Determination of the radioactivities of each recovered element by one or more appropriate counting techniques.

A useful alternative to the above involves the use of a radioactive tracer for the nuclide being determined instead of inactive carrier. The chemical yield is then determined by a suitable counting technique which distinguishes the added tracer from the nuclide being determined. This method is essential in the determination of isotopes of elements having no stable forms and may be of use in other cases. Examples are the use of ^{237}Np, which is an α-emitter, as a tracer for β-active ^{239}Np, and of ^{238}Pu as a tracer for ^{239}Pu. In the latter case the two α-emitters are determined by pulse analysis.

Perhaps the most widely known examples of radiochemical analytical procedures are those described by various authors and published in compilations edited by CORYELL AND SUGARMAN[1] and by MEINKE[2]. Since the issue of these publications numerous similar methods have been described and a number of laboratories have issued volumes of collected radiochemical procedures[3,4]. In most of these procedures, the weight of carrier element added is 10–20 mg and the chemical yield is determined gravimetrically, the final precipitate being collected and mounted in a form suitable for weighing and for counting. The whole of the recovered material is thus used for both purposes. The techniques used in the chemical separations and purifications are those of qualitative analysis using centrifugation instead of filtration; solution volumes are usually below 15 ml and rarely exceed 50 ml, most of the work being carried out in centrifuge tubes of these two sizes. The weight of the final precipitate obtained is usually in the range 10–50 mg and is spread over an area of 2–10 cm^2, the latter varying from laboratory to laboratory and depending on the window size of the β-counter used. If the compound finally weighed is of stable and reproducible composition the accuracy of such a chemical yield determination is generally within the range 0.5 to 2.0%. This is considerably better than the accuracy of the β-activity determined by means of an end-window Geiger-Müller counter, the standard instrument most used for this purpose until a few years ago, and is comparable with that of β-counting with a gas flow proportional counter under ideal conditions.

Sources of error in absolute β-counting with end-window Geiger-Müller tubes have been discussed by a number of authors[5–8] and the general conclusions at that time (1950) was that after correcting for all possible errors the accuracy attainable was not better than about 5–10%. One of the main causes of error is that due to scattering or absorption of β-particles by the solid matter associated with the source. For a given amount of activity the effect of adding increasing amounts of inactive carrier is first to increase the observed counting rate and, with larger amounts of carrier, to decrease it, so that on plotting counting rate as ordinate against source weight as abscissa a curve is obtained rising to a maximum and then falling off approximately exponentially. The initial increase in counting rate is due to scattering of β-particles in the direction of the counter window by the solid carrier material and the subsequent fall occurs when self absorption becomes sufficiently great to outweigh the primary scattering effect.

The source thickness at which the maximum occurs varies widely with the maximum energy of the β-particles emitted. Consequently, the correction factors for a particular weight of carrier also vary widely with the β-particle energy. As an example the ruthenium isotopes ^{103}Ru (0.217 MeV) and ^{106}Ru (2.00 to 3.53 MeV from ^{106}Rh daughter) may be mentioned. The correction factors in a particular set-up for 20 mg/cm^2 of a ruthenium source containing these species were 2.06 and 0.78 respectively.

The accuracy of a radiochemical determination cannot be better than those of the correction factors, and experience showed that the accurate determination of these was a matter of some difficulty. In view of the variation and inaccuracy of such factors, therefore, it was decided that an effort should be made to reduce the weights of radioactive sources to a minimum. One way of doing this is to take sufficient of the original active sample so that a small aliquot of the separated and purified nuclide gives, on evaporation, a virtually weightless source. The chief disadvantage of this procedure is the large initial sample needed. The main bulk of each species separated must be used for the gravimetric chemical yield determination and the highly active dry precipitates so obtained could constitute undesirable sources of laboratory contamination and possible health hazard. In the case of samples of low activity this procedure is not possible as it is then necessary to count most of the recovered material.

From the above considerations it was decided that the best solution lay in the reduction to a minimum of the amounts of carrier used in radiochemical separations. We therefore investigated the feasibility of carrying out such separations using 0.5- to 1-mg amounts of carrier and it is the purpose of this paper to consider the problems that arise and to describe the experimental methods that we have used under these conditions.

EXPERIMENTAL

Separations on the 1-mg scale

Preliminary experiments were carried out involving the separation of the constituents of an inactive mixture of 1 mg of each of the elements, strontium, zirconium, molybdenum, silver, barium and cerium by conventional precipitation procedures.

Silver was first separated as chloride and cerium and zirconium hydroxides precipitated with ammonia. After the hydroxides had been dissolved in dilute nitric acid, cerous fluoride was precipitated by the addition of ammonium fluoride and zirconium recovered from the supernate by precipitation with ammonia after fuming with perchloric acid to remove hydrofluoric acid.

The ammoniacal solution of barium, strontium and molybdenum was treated with ammonium carbonate to precipitate barium and strontium. Molybdenum was then precipitated with α-benzoinoxime after acidification, and the barium and strontium separated by dissolving the carbonates in a little hydrochloric acid and precipitating barium chloride with a solution of 5 vols. concentrated hydrochloric acid and 1 vol. ether.

Each separated element was then subjected to an appropriate radiochemical purification process by the methods of HUME, GLENDENIN, BALLOU AND BOLDRIDGE[1]. Volumes of all solutions and quantities of reagents used were reduced to 1/10 or 1/20 of those specified in the original methods according to whether these employed 10 or 20 mg carrier.

No difficulties were experienced in these experiments which employed only precipitation reactions. Since then separations on the milligram scale have been carried out on a large number of elements, including most of the fission products, and we have found that ion-exchange and solvent extraction techniques, where applicable, to be particularly suitable at this level.

The techniques used with 1-mg quantities of carrier do not differ markedly from larger scale procedures. As solution volumes are 1/10 or less of those used for 10-mg amounts, most of the work can be done in 3-ml centrifuge tubes, though 10-ml tubes may be needed in the earlier stages of an analysis of a mixture of radio-nuclides and for the handling and efficient washing of bulky precipitates such as molybdenum α-benzoinoxime. We have found 10 × 75 mm test tubes to be very convenient and these are used in conjunction with a Eureka centrifuge. This is a simple and inexpensive centrifuge which takes two tubes and has the advantage of very rapidly reaching full speed form rest and *vice versa*. The speed is not very high but is adequate for most purposes. Where a high speed is necessary to separate a fine precipitate the Baird and Tatlock Angle Head Centrifuge is used. This takes 6 tubes and gives a maximum speed of 10,000 r.p.m.

Solvent extractions using about 1-ml volumes of solvent and aqueous phases may be carried out conveniently in 3-ml tubes. For extractions which proceed rapidly (*e.g.* uranium into ether, metal diethyldithiocarbamates into chloroform) sufficient agitation is given by the device known variously as a transfer pipette, fountain pen filler or "spitzer", *i.e.* a glass tube drawn out into a jet at one end and fitted with a rubber teat at the other. Slow extractions (*e.g.* complexes of thenoyl-trifluoracetone into benzene) are carried out in sealed polythene ampoules which are mechanically shaken[9]. Ion-exchange separations are generally carried out on columns 4–5 cm long and

4 mm in diameter, which are convenient for handling quantities varying between tracer and 1 mg as there is seldom more than a total of 4 mg of mixed carriers actually adsorbed on a column in one experiment. The most generally useful system involves Amberlite CG 400 anion resin and hydrochloric acid solutions, and a great deal of information about the behaviour of elements in this system is due to the work of KRAUS AND NELSON[10]. Such separations utilise large differences in distribution coefficients between elements and need only the simplest of apparatus.

Determination of chemical yield and source preparation

The feasibility of radiochemical separations and purifications with 1-mg amounts of carriers having been demonstrated the problem of determining chemical yields remained to be solved before it was possible to use the procedure for quantitative work. This problem had to be considered in relation to the method of source preparation.

When the work was started it was considered desirable to minimise back-scattering of β-particles by mounting sources on a light backing and for this purpose 0.0005 inch distrene foil, having a superficial density of 1.5 mg/cm^2 was used. This is stretched over a 1-inch diameter circular hole in a $3 \times 3^3/_8$ inch aluminium card and attached to the latter by adhesive. Sources are prepared by evaporation of known amounts of an aqueous solution of the radioactive material on the distrene, a small amount of insulin being used to spread the solution over a circle of about $\frac{1}{2}$ inch diameter. At a later stage β-counters were calibrated for various emitters by direct comparison with 4π gas and proportional counting and back scattering was no longer important. However, the above method of source preparation was found to be so convenient and the resulting sources proved to be so rugged that the procedure has been continued and is still in use.

Out of an initial 1-mg carrier added, up to about 0.5 mg may be present on the active source finally prepared. Even at this level the effect of solid source material on the β-count rate cannot be neglected and it is therefore still necessary to determine correction factors over a range of source weight for each nuclide counted. For weights between 0.5 mg and zero these factors are usually between 0.9 and 1.0; if sufficient activity is available sources containing less than 100 μg carrier may be prepared and here correction factors are very nearly unity. It is evident that the classical method of counting and determining the chemical yield gravimetrically on the same precipitate is not possible under these conditions. Counting and chemical yield determinations must, therefore, be carried out on different portions of the purified material. If the separated activity is low it may be necessary to count as much of the sample as possible. This only leaves, at the most, about 200 μg of carrier for chemical yield determination and it is therefore desirable that the chemical yield methods should be sufficiently sensitive to determine a few tens of micrograms of each element with an accuracy of 1 or 2%. The procedures should be quick and simple to carry out so that it is possible to do replicate determinations with the minimum of time and trouble.

The above requirements have been met by spectrophotometric and micro-titration procedures, the latter employing spectrophotometric end-point detection. It is, of course, desirable that the method used for a chemical yield determination should be specific for the element concerned. This is not always possible, however, and then it becomes necessary to use the same method for a number of different elements. In such case one must rely heavily on the radiochemical purification process to remove interfering elements. This is generally adequate for the purpose but, if not, it may be necessary to introduce a step designed to remove a specific contaminant which may have been present in the original sample or introduced in the course of the radiochemistry. The possibility of impurities in the reagents used must also not be overlooked.

After purification of an element the material is finally obtained in solution, the total volume of which is adjusted to between 0.1 and 6 ml according to the total activity present. Occasionally it may be necessary to prepare a dilution if the activity is sufficiently high. Originally, portions for counting and chemical yield were measured by micro-pipette but it was soon found that the use of a weight burette in conjunction with a damped, weight-loading balance afforded a rapid, accurate and much more flexible method of dispensing solutions. The most convenient vessel for use as a weight burette has been found to be a blown polythene ampoule[9] with the neck drawn out into a capillary jet. The weight is about 2 g and the volume held about 6 ml. Filling and emptying are easily effected by squeezing and very fine control of delivery of drops is possible. The contents may be stored without loss by evaporation if the end of the jet is closed by means of a pair of tweezers whose tips have been heated for a few moments in a flame.

The same type of vessel is used for storing carrier solutions which are also dispensed by weight. These are prepared at a concentration of 10 mg of element per g of solution and from each an accurate dilution containing 200 μg per g is prepared. The dilute solution is stored in a sealed 50-ml polythene ampoule and portions are weighed out for standardisation at the same time as chemical yield samples.

Chemical yield determinations involve purely relative measurements and absolute standardisation of carrier solutions is not, therefore, necessary. The weight of carrier on the source may be required for determining the counting correction factor due to finite source weight but as this only needs to be known to about 10%, it would be sufficient to prepare the carrier solution to this accuracy. In spite of this we consider it desirable that carrier concentrations should be known to at least 1%, as this enables a constant check to be maintained on the functioning of the methods. Consequently, wherever possible, carrier solutions are prepared accurately by weight from suitable standard compounds having compositions known to be within 1% of theoretical. In other cases (*e.g.* ziconium) the carrier solutions are standardised by a suitable gravimetric method.

Spectrophotometric methods

The accuracy of a spectrophotometric procedure depends on the absorbancy of the solution being analysed and it may be shown[11] that, if Beer's Law is obeyed, it is a maximum at an absorbancy of 0.434 and varies only slightly between 0.2 and 0.7. This calculation is based entirely on the relation between absorbancy and the deflection of the null indicating instrument of the spectrophotometer. To minimise blank errors we prefer to keep absorbancy readings high rather than low and aim at values between 0.4 and 0.7. In designing a chemical yield method, therefore, the final volume of coloured solution and the cell length are chosen to give absorbancies in this range with a few tens of micrograms of element.

The instrument used for most measurements in a Unicam SP600, a glass prism spectrophotometer operating between 360 and 1000 mμ. The 4-cm cell needs a minimum of 8 ml solution and the largest volumetric flask which need be used, therefore, is a 10-ml.

A list of spectrophotometric methods which have been found suitable for chemical yield determinations is given in Table I together with other relevant information and references.

TABLE I

SPECTROPHOTOMETRIC METHODS

Element	*Method*	*Solution volume (ml)*	*Cell length (cm)*	*μg Element for absorbancy of 0.5*	*Wave length (mμ)*	*References*
P	Molybdenum blue	25	1	38	830	16
V	Phosphotungstic acid	10	4	34	400	16
Mn	Periodic acid	10	2	57	525	17
Fe	Thioglycollic acid	25	4	37	550	16
Co	Thiocyanate	10	4	45	620	16, 18
Ni	Dimethylglyoxime	25	2	36	450	16
Ge	Molybdenum blue	25	4	36	830	16
As	Molybdenum blue	25	1	38	830	16
Y	Bromopyrogallol red	25	1	23	660	19
Zr	Quercetin	25	1	42	440	20
Mo	Thioglycollic acid	25	4	56	365	21
Ru	Dithio-oxamide	25	4	36	650	16
Rh	Stannous chloride	10	4	42	480	16
Sn	Morin	20	2	56	430	22
Sb	Iodide	10	4	50	425	16, 23
Ce	Bromopyrogallol red	25	1	31	680	19
Rare earths	Bromopyrogallol red	25	1	36	660	19
Au	Hydrobromic acid	10	4	63	380	16
Bi	Iodide	25	4	30	460	16

Micro-titration methods

In titrations at the microgram level the indicator blank is a substantial fraction of the total titration and judgement of the end-point is difficult. Consequently instrumental procedures must be used, and we have employed potentiometric and spectrophotometric end-point detection. Micro-burettes of the micrometer syringe type are convenient and accurate and we have generally used the "Agla", made by Burroughs Wellcome Ltd. A maximum volume of 0.5 ml of solution may be delivered and the accuracy of rading is 0.0002 ml. In use, the glass jets supplied by the makers are replaced by home-made polythene ones which have the advantages of not being wetted by aqueous solutions and of being unbreakable.

A potentiometric end-point is employed in the determination of silver by titration with 0.002 *M* potassium iodide and of iodine as iodide by titration with 0.002 *M* silver nitrate. The bimetallic electrode system of CLARK[12] is used, consisting of two silver wires, one of which is amalgamated. The potential change at the end-point is due mainly to the sluggishness of the response of the amalgamated electrode to changes in silver ion concentration. The titration is carried out in 2–3 ml of 0.1–0.2 M nitric acid solution which is contained in a 5-ml tall form beaker and stirred magnetically.

The Schwarzenbach method, adapted for spectrophotometric operation, is used for the determination of calcium, strontium, zinc, cadmium, barium and lead, the element being titrated with 0.0025 M disodium dihydrogen ethylene-diaminetetracetate (EDTA) using Solochrome Black W.D.F.A. (Eriochrome Black-T) as indicator. The titration is carried out in about 7 ml of ammoniacal solution in the presence of magnesium–EDTA complex to ensure an adequate colour change in the titration of barium and strontium which give only weak complexes with the indicator. In the titration of lead a little ammonium tartrate is added to prevent hydroxide precipitation.

The wave length used is 550 mμ, at which the absorption by the metal indicator complex is a maximum. The initial absorbancy, when all the indicator is combined with metal, is measured and the solution titrated to an absorbancy of 0.75 times this value. At the end-point half of the indicator is combined with metal and half is uncomplexed. If no volume change occurs the ratio of the initial to end-point absorbancy has been found to be 0.78, and the factor 0.75 includes a correction for the volume change during titration.

The titration unit, designed to fit into the cell carriage compartment of the SP600 is shown in Figs. 1, 2 and 3. It is constructed mainly of $^1/_8$-inch perspex sheet, blackened on the top surfaces to exclude stray light from the interior of the instrument, and consists of two main parts A and B, with a perspex cell C which has a light path of 2 cm and is 3 cm high and 1.8 cm wide.

Part A, the upper assembly, carries the cell and Agla burette. The end of the plunger and face of the micrometer are held in contact by the tension of a thread fastened

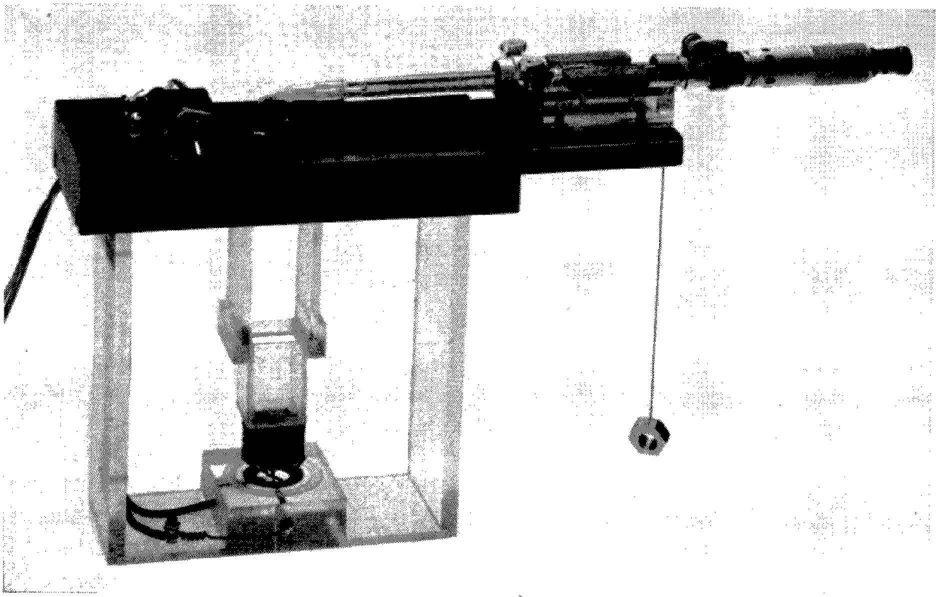

Fig. 1. Micro-titration unit assembled for use.

at one end to a collar holding the plunger and which passes over a cylindrical nut and supports a weight hanging at the other end. The cell C has flanges along two of its upper edges which slide into grooves provided in the holder attached to the bottom of A. Part B, the lower assembly, fits into the cell carriage compartment of the spectrophotometer and remains in position during a series of titrations. In its base is fitted a magnetic stirrer shown in Fig. 3, consisting of a small 3–4 V electric motor (the "Electrotor" Type 240 is suitable) which is mounted upside down and held by its

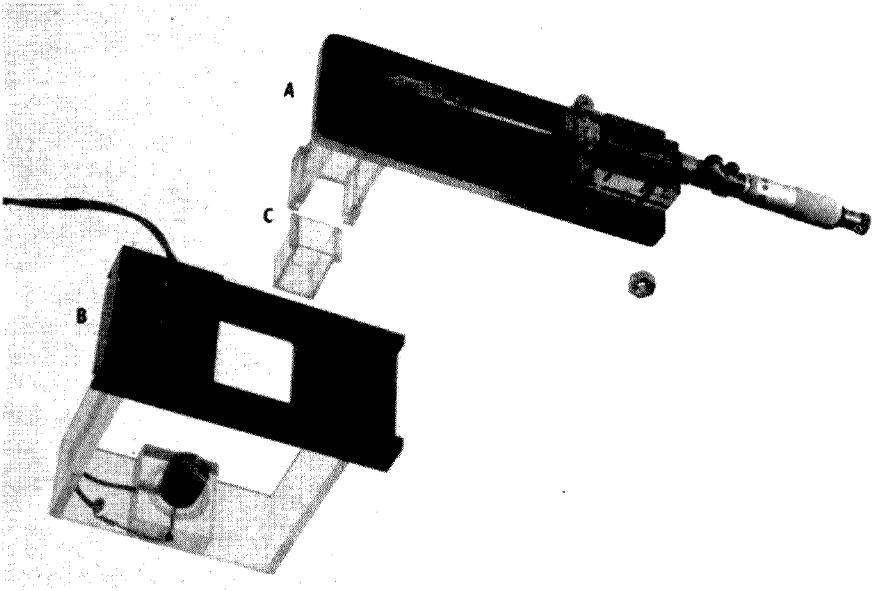

Fig. 2. Micro-titration unit showing the component parts A, B and C.

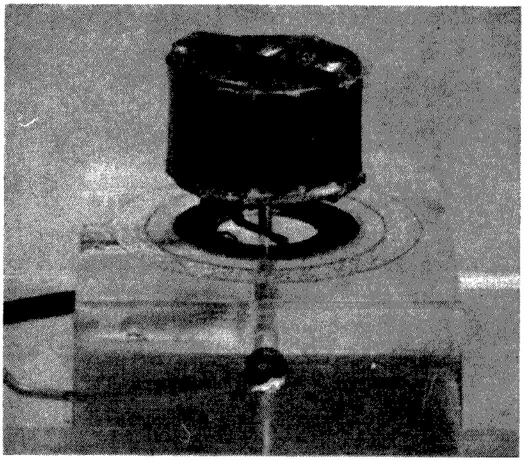

Fig. 3. Micro-titration unit. Enlarged view of magnetic stirrer.

spindle. A piece of phosphor bronze strip is soldered to one of the two motor contacts and brushes the surface of a brass ring set into a perspex block which also holds the spindle. The other contact is made via the grub screw holding the spindle in the perspex block, the spindle itself and a strip of brass soldered to the top of the motor and in rubbing contact with the top of the spindle. Also attached to B are the switch and variable speed control resistance which are connected in series with a 3-V battery and the motor via the brass ring and spindle. When the current is switched on the motor body rotates around the spindle, and rotation of the field magnet drives the stirrer, which consists of a short piece of steel wire sealed in polythene, at the bottom of the cell.

When the unit is in position inside the SP600 the light beam passes centrally through the cell, the bottom of the beam being well clear of the rotating stirrer and burette jet.

Accuracy of radiochemical procedures and chemical yield methods

The coefficients of variation of radiochemical procedures for determining ^{99}Mo, ^{111}Ag, ^{115}Cd and ^{140}Ba using 0.5 to 1 mg of carrier are given in Table II. These have been calculated from the results of 2 to 11 replicate determinations on a number of different samples of solutions of mixed fission products. Similar calculations have been made for some chemical yield methods using the results of 2 to 4 replicate determinations on carrier and on the purified active solutions obtained after radiochemical separations. These results are also given in Table II.

TABLE II

COEFFICIENTS OF VARIATION OF CHEMICAL YIELD METHODS AND OF COMPLETE RADIOCHEMICAL PROCEDURES

Element	*Chemical yield procedure*			*Nuclide*	*Complete radiochemical procedure*		
	μ	k	Σn_i		μ	k	Σn_i
Co	1.2	22	56				
Ni	1.2	33	67				
Sr	1.1	61	134				
Y	1.2	48	103				
Zr	1.2	39	97				
Mo	1.0	56	119	^{99}Mo	3·6	36	221
Ru	1.1	34	80				
Ag	0.8	51	114	^{111}Ag	3·4	22	101
Cd	1.0	67	143	^{115}Cd	5·1	32	164
Ba	1.0	71	146	^{140}Ba	5·6	34	172
Ce	1.0	61	139				
Rare earths (Pr, Nd, Sm, Eu, Gd, Tb)	1.0	64	133				

The figures are realistic and were obtained in routine analyses; 18 different chemists were concerned in the radiochemistry and 9 in the chemical yield determinations.

The method of calculation was a follows: From each set of replicates on each sample the standard deviation was calculated and hence the coefficients of variation. The normal method of calculation was used for 4 or more observations but when only 2 or 3 results were available the method of small number statistics[13] was used. This involves multiplying the range by 0.89 or 0.59 for 2 or 3 results respectively to give the standard deviation, and gives a rather higher figure than the normal method.

If μ_i ($i = 1$ to k) are the individual values of the coefficient of variation, each being calculated from n_i observations, then the best value of the coefficient of variation μ is given by[14]

$$\mu = \sqrt{\frac{\Sigma n_i \mu_i^2}{\Sigma n_i}}$$

where Σ signifies summation between the limits of $i = 1$ and $i = k$. k is the number of different samples examined and Σn_i the total number of determinations made. μ is the coefficient of variation of a single determination.

The chemical yield determination involves replicate determinations of the concentrations of two solutions, the carrier and the final active solution, and a calculation involving the ratio of the two concentrations. Using the normal formulae for determining the standard deviation of arithmetically combined quantities it is readily shown that the coefficient of variation of a chemical yield is about equal to μ when the determination of each concentration is carried out in duplicate, and less than μ when more replicates are done. In general, therefore, we should not expect the coefficient of variation of a chemical yield to be worse than the values given in Table II.

The radiochemical procedures used were those of GLENDENIN AND BALLOU[1], and most of the measurement of β-activity were made with gas flow proportional counters of either 4 π or end-window type, a 9:1 mixture of argon and methane being used as counting gas. Some results from Geiger-Müller counters are also included. Under our conditions of use, in which frequent checks were made with long lived standard sources (^{204}Tl) and appropriate corrections made for counter variation, no significant difference in accuracy between the Geiger-Müller and the more stable proportional counters was observable.

The results for the radiochemical determinations of ^{99}Mo, ^{111}Ag, ^{115}Cd and ^{140}Ba show that the contributions made to the overall errors by the chemical yield procedures are insignificant. We attribute the major source of error to β-counting. Recent results[15] of careful intercomparison of 4 π β-counting techniques between various laboratories in the U.K., Canada and U.S.A. gave coefficients of variation of up to 3%. This work was carried out with virtually carrier free sources of ^{60}Co, ^{22}Na and ^{90}Sr–^{90}Y and we would expect a greater variation than this under our routine conditions with rather thicker sources.

DISCUSSION

The micro-techniques for radiochemical analysis described above have been in routine use in this Establishment since 1954. The reasons for their adoption have been dealt with in the Introduction but in use other advantages quickly became apparent. These are:

(*a*) Reduction in space and volumes of reagents needed. This is of particular value in utilising space in active fume cupboards which never seem to be large enough for radiochemical work.

(*b*) Elegance and speed. The use of small volumes of solution saves time, particularly in evaporation.

(*c*) Flexibility and replication. By weighing out portions of the final solution optimum amounts for counting and chemical yield may be obtained. Also, errors may be minimised by replication of chemical yield determinations and preparation and counting of sources.

(*d*) Adequate accuracy of chemical yield determination even when the yield is very low, as occasionally happens. In the worst cases all the material may be counted and the chemical yield determined on the source when this is finished with.

(*e*) If α-emitters are to be determined on the same sample it is of advantage to have the minimum total solid material present to ensure the production of as thin α-sources as possible.

Difficulties could arise in the application of these techniques in exceptional circumstances. The only case we have experienced has been in the determination of active strontium isotopes in occasional samples containing much calcium, when the radiochemical procedure has not been quite adequate to remove all the calcium, giving erroneously high chemical yields. This can be overcome by modifying the procedure, but the radiochemical analysis of any samples containing much solid material should be carefully considered to ensure adequate chemical as well as radiochemical purification. The possibility of the presence in the sample of the stable forms of radio-nuclides being determined should be borne in mind also, as erroneous chemical yields could result. In such cases chemical determinations of the elements in question must precede radiochemical analysis.

The further reduction of carrier weight by a factor of 10 would allow the virtual elimination of source weight corrections in β-counting in all but the very softest of emitters. At the 100-μg level precipitation reactions become less useful as it is not practicable to reduce solution volumes below the present minimum of 1–2 ml and hence solubility begins to limit the chemical yields attainable. One way out of this difficulty has been described by RUDSTAM[24] who carried out radiochemical separations with 100 μg carrier and used spectrophotometric methods for determining chemical yields. Precipitations were made with the help of several milligrams of non-isotopic carriers which were then separated from the wanted nuclide and its isotopic carrier at appropriate stages of the analysis. This technique is of somewhat limited application and the more extensive use of ion-exchange and solvent extraction procedures would probably be more fruitful at the 100-μg level.

Another requirement for radiochemical analysis with 100-μg quantities of carriers is greater sensitivity in chemical yield methods. To retain the desirable feature of replication of chemical yield determinations methods are required which will give the required accuracy of 1–2% with about 5 μg of element. It is hoped to describe a suitable procedure based on micro-coulometry in a forthcoming paper.

SUMMARY

Techniques used at A.W.R.E. during the past 6 years for the radiochemical analysis of mixtures of active nuclides using 0.5- to 1-mg quantities of carrier are described and their advantages discussed. Micro-methods are listed for chemical yield determinations by spectrophotometry and micro-titration, and details are given for the micro-titration of a number of elements with EDTA, using a spectrophotometric end-point. A special fitment is described to enable the Unicam SP600 spectrophotometer to be used for micro-titrations. Some values are given for the coefficients of variation obtained in typical chemical yield methods and in overall radiochemical determinations of ^{99}Mo, ^{111}Ag, ^{115}Cd and ^{140}Ba.

RÉSUMÉ

Les auteurs font un exposé des techniques utilisées au cours de ces six dernières années pour leurs recherches dans le domaine de l'analyse radiochimique de mélanges de radio-isotopes. Des microméthodes titrimétriques et spectrophotochimiques sont proposées.

ZUSAMMENFASSUNG

Es wird ein Ueberblick gegeben über die in den vergangenen 6 Jahren angewandten Methoden bei der radiochemischen Analyse von Gemischen von Radio-Isotopen mit besonderer Berücksichtigung von Spektrophotometrie und Mikrotitrationen mit EDTA.

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Short Communications

La détermination du tungstène en présence de vanadium

Dans un article précédent[1], nous avons recommandé la cinchonine et la β-naphtoquinoline comme réactifs gravimétriques pour la détermination quantitative du tungstène. Comme le vanadium est un élément du même groupe, nous avons étudié l'influence du vanadium sur cette détermination gravimétrique du tungstène.

Nous avons employé une méthode directe analogue à celle indiquée dans l'article mentionné, et obtenu les résultats suivants pour différentes quantités de vanadates en présence de tungstates.

TABLEAU I

Réactif	*Cinchonine*			*β-Naphtoquinoline*		
V/W	*mg* ↓	*mg* V_2O_5	%	*mg* ↓	*mg* V_2O_5	%
2	356.3	40.9	+13.0	354.2	38.8	+12.3
1	337.3	21.9	+ 6.9	336.8	21.4	+ 6.8
0.4	326.5	11.1	+ 3.5	325.9	10.5	+ 3.3
0.2	325.2	9.8	+ 3.1	324.7	9.3	+ 3.0
0.08	323.4	8.0	+ 2.5	322.9	7.5	+ 2.4
0.04	321.1	5.7	+ 1.8	320.6	5.2	+ 1.6

Les résultats démontrent que la présence de vanadium donne lieu à une forte coprécipitation, par laquelle les deux réactifs ne peuvent être employés dans la méthode directe.

Une coprécipitation analogue du molybdène a été observée dans un article précédent[2] et a pu être minimalisée par l'emploi d'une méthode décrite en détail dans l'article mentionné. En employant la même méthode pour des mélanges de tungstates et de vanadates, nous avons obtenu les résultats suivants (Tableau II).

TABLEAU II

V/W	*mg* ↓	*mg* V_2O_5	%
2	173.1	1.0	0.58
0.8	173.0	0.9	0.53
0.4	172.7	0.6	0.35
0.16	172.3	0.2	0.12

Ces résultats démontrent que les phénomènes de coprécipitation du vanadium peuvent être minimalisés en effectuant une double précipitation en présence d'acide nitrique et de perhydrol et en employant la β-naphtoquinoline comme réactif. De cette manière, il nous a été possible de déterminer la teneur en tungstène à 0.6% près en présence d'une quantité double de vanadium.

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[1] A. Claeys, *Anal. Chim. Acta*, 17 (1957) 360.

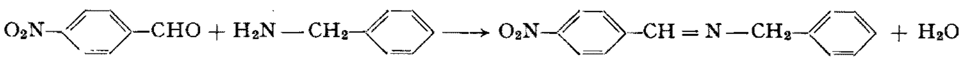
[2] A. Claeys, *Anal. Chim. Acta*, 19 (1958) 114.

Reçu le 23 janvier 1961

Spot test for benzylamine and *p*-nitrobenzaldehyde*

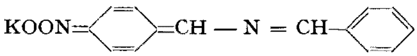
ISOMERIZATION EFFECTS THROUGH FORMATION OF A *p*-QUINOID NITRONIC ACID

If a colorless diluted alcoholic solution of *p*-nitrobenzaldehyde and benzylamine is treated with alkali hydroxide and warmed, an intense red-brown color appears. The color reaction is obviously due to the formation of the Schiff base (I) that was first isolated by INGOLD AND PIGGOT[1]:



(I)

This product undergoes prototropic rearrangement in the presence of alkalis to give a *p*-quinoid nitronic acid salt (II):



(II)

The intense color quality of (II) doubtless is due to its chain of *p*-quinoid and conjugated double bonds.

Since all of the reactions essential to the formation of the highly colored alkali salts of the *p*-quinoid nitronic acid occur rapidly and with small amounts, a spot test for the detection of benzylamine and *p*-nitrobenzaldehyde has been developed on this basis.

Detection of benzylamine

A drop of the test solution, in alcohol if possible, is treated in a micro test tube with a drop of a saturated alcoholic solution of *p*-nitrobenzaldehyde and kept at 80° in a preheated water bath. After 5 min a drop of 2% alcoholic sodium hydroxide solution is added. If the response is positive, a brown-red color appears.

Limit of identification: 10 μg benzylamine.

Considerable quantities of ethylenediamine**, *p*-aminophenol or hydrazine derivatives a free NH_2-group may not be present since they form condensation products with *p*-nitrobenzaldehyde which likewise yield colored salts of quinoid nitronic acids with alkali hydroxide.

Detection of p-nitrobenzaldehyde

A drop of the test solution is treated in a micro test tube with a drop of benzylamine and warmed for 5 min in a water bath. If *p*-nitrobenzaldehyde was present, a red

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* Translated by Ralph E. Oesper, University of Cincinnati.

** Ethylenediamine can be detected through its color reaction with rhodizonic acid[2].

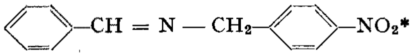
or pink color appears when a drop of 2% alcoholic potassium hydroxide solution is added.

Limit of identification: 1 µg *p*-nitrobenzaldehyde.

This color reaction is not shown by *o*- and *m*-nitrobenzaldehyde or by 2,4-dinitrobenzaldehyde.

In neither test is it permissible to use the now popular solvent, dimethylformamide, since it gives a color reaction with nitro compounds.

The chemistry of the test here described deserves attention because it leads to a case of hitherto unique isomerization. It is obvious that the salt (II) may also be obtained through prototropic rearrangement of the Schiff base of benzaldehyde and *p*-nitrobenzylamine (Ia), which is an isomer of the Schiff base (I), as shown by the following formula:



(Ia)

Consequently it was logical to expect that treatment of the alkali salt(II) with dilute acid would produce initially a mixture of the two isomeric Schiff bases (I) and (Ia), from which by acid hydrolysis there will result the regeneration of all of the compounds necessary to the production of both the isomers (I) and (Ia), namely benzylamine, *p*-nitrobenzaldehyde, benzaldehyde, *p*-nitrobenzylamine. This actually is the case as shown by the following trial with the pair *p*-nitrobenzaldehyde–benzylamine.

A micro test tube was used. Several cg of *p*-nitrobenzaldehyde and benzylamine in alcohol were warmed briefly; alkali hydroxide was added, and the system was then allowed to stand for 1 h. The resulting brown-red solution was then warmed to 40° along with dilute hydrochloric acid, and the mouth of the test tube was covered with a disk of filter paper moistened with an ether solution of benzidine. A yellow stain appeared on the reagent paper; it was due to the Schiff base formed from the benzidine and the benzaldehyde vapors. *p*-Nitrobenzaldehyde does not volatilize under these conditions.

The isomerization through formation of alkali salts of quinoid nitronic acids and their acid decomposition indicates possibilities for preparation procedures directed toward the obtaining of substituted *p*-nitrobenzylamines.

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[1] CH. K. INGOLD AND H. A. PIGGOT, *J. Chem. Soc.*, 121 (1922) 2385.
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* This Schiff base has also been isolated by INGOLD AND PIGGOT[1]. Its melting point is 71°, in contrast to 56° of its isomer.

Observations on the thermal decomposition of cupric acetate monohydrate

The thermal decomposition of cupric acetate monohydrate has been studied thermogravimetrically by Duval[1]. The elimination of water of hydration was shown by a weight loss starting at 107° and concluding at 167°. Further, a complex reaction was reported which was interpreted to result in the formation of copper and cupric oxide, and was initiated at 270° and was complete by 296°. A subsequent slow weight gain up to 510° was associated with the oxidation of metallic copper.

This reaction appeared to be unusual as the copper coexisted in the divalent state and as the free metal. The application of other techniques — differential thermal analysis, X-ray analysis, and mass spectrometry — to the phenomenon could shed more light on the thermal decomposition.

EXPERIMENTAL

The differential thermal analysis apparatus employed was of two types: (*1*) that manufactured by the R. L. Stone Co.[2], Austin, Texas, and (*2*) that described by Hill, Schacher and Murphy[3]. The latter equipment permitted the analysis of the gaseous products evolved during the reaction to be collected and analyzed. Good agreement was obtained with thermograms produced with both equipments. The thermograms were obtained from approximately 20 mg of material employed as a sandwich in alumina. Heating rates of approximately 10° per minute were employed. An air atmosphere was employed in all cases, the pressure being approximately 0.5 mm. X-ray diffraction patterns were obtained on a General Electric Model XRD-5 X-ray spectrograph. Gas analyses were performed using a General Electric Analytical Mass Spectrometer. Materials employed were of a C.P. grade.

DISCUSSION

The thermogram of cupric acetate monohydrate, Fig. 1, shows the release of water of crystallization starting at about 145° and peaking at approximately 180°. A series

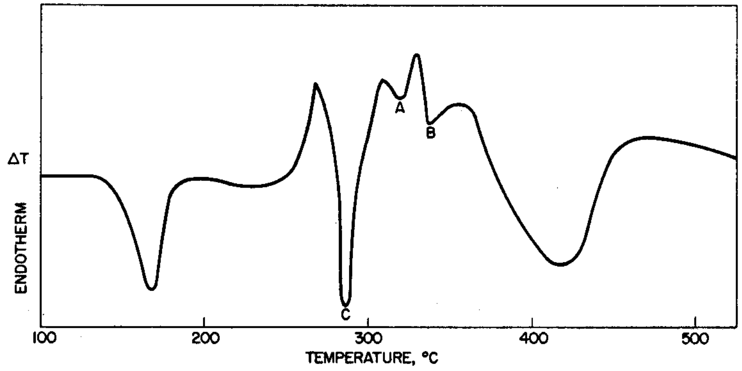

Fig. 1. Differential thermogram, cupric acetate monohydrate.

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of complex reactions were initiated in the range 245–450°. Thermograms for cupric oxide and its 50–50 mole % mixture with copper showed no thermal effects in the temperature range covered by Fig. 1.

A gas sample was obtained from the second differential thermal analysis apparatus at point C indicated on the thermogram. The mass spectrum indicated the gas to be principally carbon dioxide with a substantial amount of water. Very small quantities of acetone and methane were also present. It was interesting to observe that there was no residual oxygen in the air background, indicating occurrence of an oxidation reaction with the unusual decomposition.

X-ray analyses were made of sample holder residues obtained by stopping the differential thermal runs at points A and B. The residue at B gave only lines corresponding to cupric oxide. At point A, the X-ray diffraction pattern corresponded to a mixture of cuprous oxide and copper metal.

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[1] C. DUVAL, *Anal. Chim. Acta*, 20 (1959) 264.
[2] R. L. STONE, *J. Am. Ceram. Soc.*, 35 (1952) 76.
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Separation of niobium and tantalum by N-benzoyl-N-phenylhydroxylamine

N-Benzoyl-N-phenylhydroxylamine was used by MAJUMDAR AND MUKHERJEE[1] for the separation and gravimetric determination of niobium and tantalum. They recommended a pH range of 3.5 to 6.5 for the complete precipitation of niobium and a pH below 1.5 for the precipitation of tantalum from tartrate solutions.

TABLE I

pH of pptn. of Nb	*Nb_2O_5 taken, mg*	*Ta_2O_5 taken, mg*	*Coagulation period, min*	*Wt. of Nb complex, mg*	*Nb_2O_5 found, mg*	*Ta_2O_5 found, mg*
3.0	8.7	12.7	30–35	—	8.2	12.84
3.5	8.7	12.7	30–35	48.4	8.635	12.6
4.0	8.7	12.7	30–35	48.6	8.67	12.6
4.0	12.4	5.4	30–35	—	12.40	5.4
4.5	8.7	12.7	25–30	48.8	8.7	12.68
5.0	8.7	12.7	25–30	48.8	8.7	12.73
5.5	8.7	12.7	25–30	48.83	8.7	12.70
6.0	8.7	12.7	25–30	48.6	8.67	12.72
6.5	12.4	5.4	30–35	—	12.2	5.0

In a recent communication[2], LANGMYHR AND HONGSLO suggested that the pH range could profitably be narrowed from 3.5–6.5 to 4.5–5.0; this latter pH range is said to give better results for separation while the former may cause precipitation of hydrous oxide and needs a longer coagulation period. We have now checked that the pH range, as suggested by MAJUMDAR AND MUKHERJEE, gives quite good results within the specified coagulation period; moreover, there is no possibility of the precipitation of hydrous oxide, even when the niobium or the tantalum solution is made ammoniacal. The results shown in Table I confirm these observations.

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[1] A. K. MAJUMDAR AND A. K. MUKHERJEE, *Anal. Chim. Acta*, 19 (1958) 23; 21 (1959) 245.
[2] F. J. LANGMYHR AND T. HONGSLO, *Anal. Chim. Acta*, 22 (1960) 301.

Received November 26th, 1960

Anal. Chim. Acta, 24 (1961) 497–498

Voltammetric determination of antioxidants at the wax-impregnated graphite electrode

The wax-impregnated graphite electrode is well-known in the analysis of antioxidants[1–4]. A real improvement was suggested by MORRIS AND SCHEMPF[4], who made very reproducible electrode surfaces on a manual lathe.

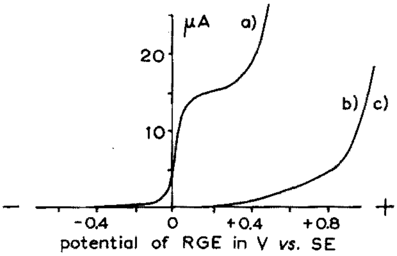

Fig. 1. Anodic oxidation of 2,6-di-*tert.*-butyl-*p*-cresol at the RGE in (a) basic solution, (b) weakly acidic solution, and (c) acidic solution. See text for compositions. RGE = Rotating wax-impregnated graphite electrode; SE = Silver–silver chloride electrode.

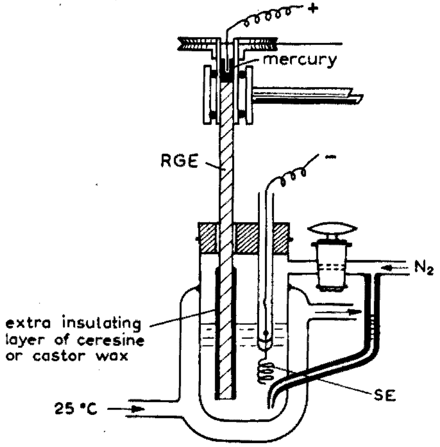

Fig. 2. Voltammetric cell. RGE, SE — see legend to Fig. 1.

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As far as we know, investigation of the influence of the pH on the mechanism of oxidation at the electrode has been limited to the lower pH values. A possible explanation for this may be that the anodic potential range is much smaller in basic than in acidic or neutral supporting solutions. However, the oxidation potentials of anti-oxidants of both the phenolic and the amino type are shifted in the same sense (*i.e.* more negative at higher pH-values), since hydrogen ions are always involved in the anodic oxidation process. Therefore, in most cases a supporting electrolyte of higher pH can be used and recommended, especially for anti-oxidants of the phenolic type because the reaction becomes more reversible, with the result that the wave form is considerably improved (see Fig. 1).

Rotation of the electrode at a speed of *ca.* 500 rev./min affects both the reproducibility and the sensitivity favourably (see Fig. 2 for instrumental details). Under these conditions the wave form equals the normal polarographic form, whilst concentrations down to $5 \cdot 10^{-7}$ *M* can be detected.

EXPERIMENTAL

Composition of the supporting electrolyte

(*a*) Place 5 ml of $5 \cdot 10^{-4}$ *M* 2,6-di-*tert.*-butyl-*p*-cresol in methanol, 3 ml of lithium chloride (5 g per 100 ml methanol) and 5 ml of 0.1 *M* potassium hydroxide in methanol in a 25-ml volumetric flask. Fill up with methanol.

(*b*) and (*c*) Prepare the solution as described in (*a*) with the exception of the potassium hydroxide. Replace the latter by 5 ml of 0.1 *M* boric acid in methanol (*b*) or by 0.5 ml of 0.1 *M* hydrochloric acid in methanol (*c*). The water content of the methanol should be as low as possible.

Summary of the analytical procedure

Rate of polarization: 0.8 to 0.9 mV per sec. Temperature: 25.0°. Polish the electrodes before each determination with a fine grade of sand paper. Precondition the RGE for 2 min at +0.9 V *vs.* SE((weak)-acidic supporting electrolyte), or at +0.5 V *vs.* SE (basic supporting electrolyte). Removal of oxygen is not essential. Electrolyse the solution to more positive values.

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[1] V. F. GAYLOR, A. L. CONRAD AND J. H. LANDERL, *Anal. Chem.*, 29 (1957) 224, 228.
[2] P. J. ELVING AND A. F. KRIVIS, *Anal. Chem.*, 30 (1958) 1645.
[3] R. A. NASH, D. M. SKAUEN AND W. C. PURDY, *J. Am. Pharm. Assoc., Sci. Ed.*, 47, No. 6, June (1958) 433, 436.
[4] J. B. MORRIS AND J. M. SCHEMPF, *Anal. Chem.*, 31 (1959) 286.

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Revue de livre

Electrochimie Théorique par EUGÈNE ET GENEVIÈVE DARMOIS, Masson & Cie., Paris, 1960, ii + 240 pp., 123 Figs., cartonné toile demi-souple, 39NF.

Bien que sous forme relativement succinte, ce livre est indiscutablement destiné au succès. Il contient l'étude de tous les phénomènes dans lesquels la présence ou le transport de charges électriques sont associés à la matière, quel que soit son état, solide, liquide ou gazeux, qu'elle se présente sous une forme simple, telle que les solutions ou les sels fondus, ou sous une forme plus complexe, telle que les électrolytes colloïdaux.

Les auteurs, loin de se contenter d'exposer tout simplement les données de la bibliographie, procèdent à un examen critique et éclairé des diverses théories en se basant sur un grand nombre de travaux, tout à fait remarquables d'ailleurs, effectués dans leurs laboratoires.

Nous ne pouvons donner ici que les grandes divisions de l'ouvrage: Historique; Conductibilité des électrolytes, sa mesure; Conductibilité équivalente; Mobilité des ions, nombres de transport; Mobilité des ions et viscosité; Force électromotrice des piles, coefficient d'activité des électrolytes; Anomalies des électrolytes forts, dissociation; La théorie de l'interaction ionique et ses perfectionnements; Propriétés irréversibles des électrolytes; Propriétés optiques des solutions électrolytiques, degré de dissociation des électrolytes d'après les méthodes optiques; Propriétés des électrolytes fondus; Retour sur les F.E.M. des piles, électrodes du premier genre, potentiels normaux; Électrodes du deuxième et troisième genres, applications diverses; Piles avec et sans diffusion, diffusion des électrolytes; Étude de la concentration en ion hydrogène; Électrolytes colloïdaux et applications; Électrolytes solides semiconducteurs; Polarisation des électrodes, mesure de la F.E.M. de polarisation, polarographie; Surtension d'activation, dégagement des gaz et dépôt des métaux; Anodes solubles, passivité; Double couche au contact d'un métal et d'un électrolyte, électrocapillarité; Phénomènes électrocinétiques, électroosmose, électrophorèse, applications; Électrochimie des gaz; Applications analytiques de l'électrochimie; Galvanoplastie et dépôts métalliques; Technique des différents dépôts galvaniques.

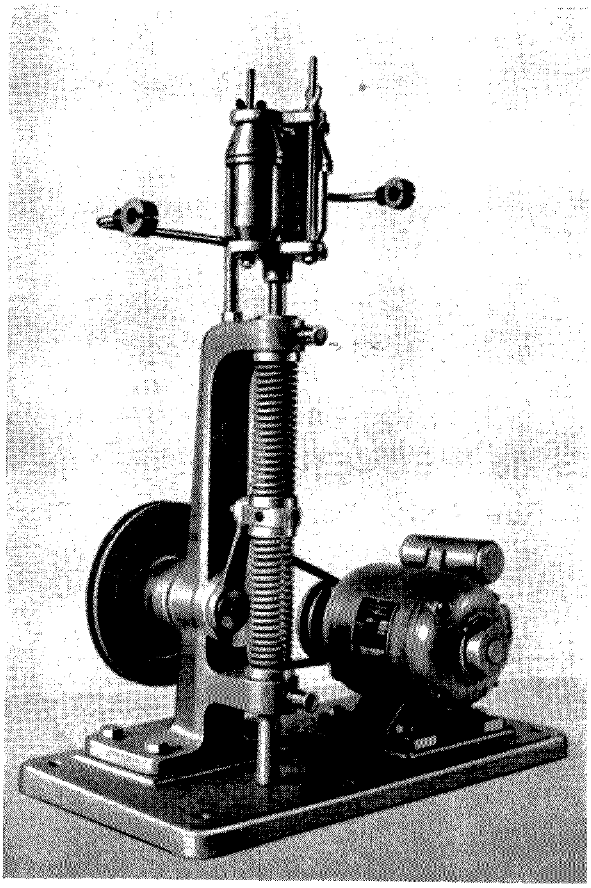
Pour terminer, nous nous faisons un plaisir de signaler que l'*Electrochimie Théorique* d'EUGÈNE et de GENEVIÈVE DARMOIS est un livre qui, grâce à son caractère vivant, incite à la reflexion et que, par cela même, il pourra donner des nouvelles idées fécondes aux chercheurs dans cette branche, auxquels EUGÈNE DARMOIS ne peut, hélas! plus se joindre. Qu'il nous soit permis de rendre un hommage ému à la mémoire du grand chercheur que fut ce savant.

Une recommandation du livre serait superflue, car ceux qui l'ont déjà étudié ne pourraient que très difficilement s'empêcher de s'exprimer en faveur d'une oeuvre aussi remarquable.

I. KAPÉTANIDIS (Genève)

A GRINDER

for the analyst



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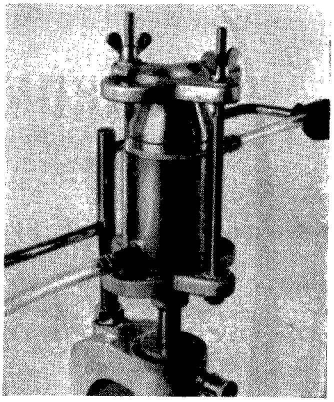
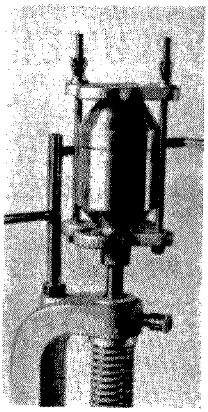
- Cement and clinker, Sand, Earth and rock, Pebbles, Ores.
- Treponemes, Vitamin B 6, Lactic ferment.



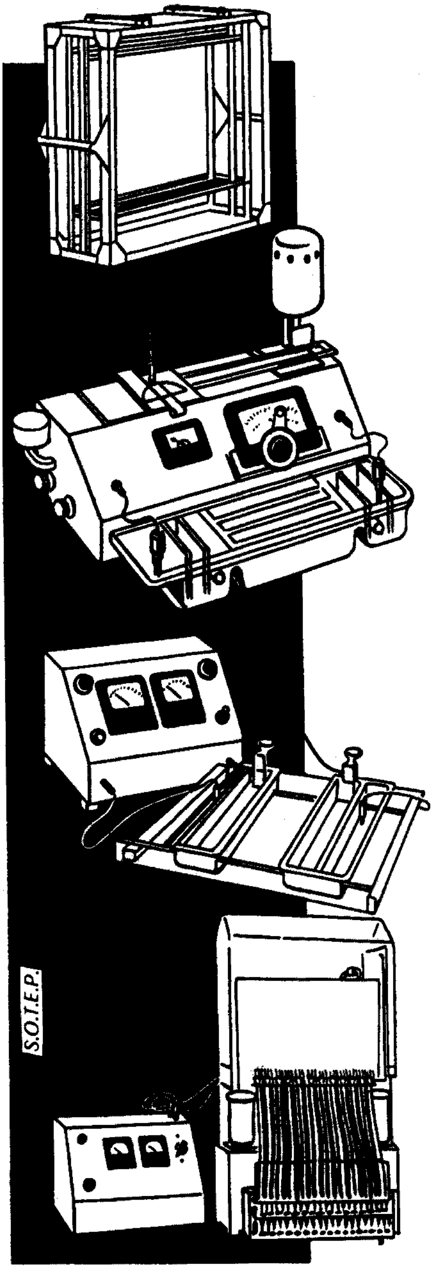
▲ *65 ml pot with cooling circulation*

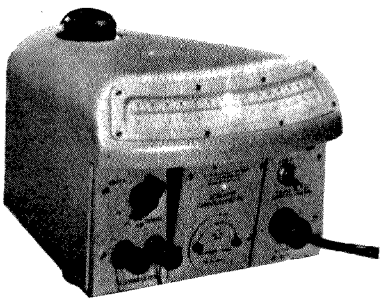


◄ *150 ml grinding pot*

PROLABO

12, Rue Pelée PARIS XI^e


S.O.T.E.P.



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GALVANOMETERS

A critically-damped galvanometer provides maximum convenience in use. Under ideal conditions the light spot is deflected to its reading position positively and allows accurate readings to be taken at a glance. To achieve these conditions a galvanometer should be selected so that its critical damping resistance matches as closely as possible the external circuit resistance, avoiding the necessity of shunting or padding the external circuit with a series resistor to attain critical damping. In this way maximum available power reaches the coil, ensuring maximum sensitivity. Twelve models of the "Scalamp" Galvanometer are available as listed below and these provide a choice for a wide range of external circuit conditions.

Model	Resistance (ohms)	Terminal resistance with shunt (ohms)	Critical damping resistance (ohms)	Typical sensitivity		
				(mm/μA)	(mm/μV)	(μA/mm)
7890/S	23	23	10	12	0.52	0.083(Direct)
7891/S	25	20	100	20	1.0	0.05
7892/S	90	90	1000	65	0.72	0.015
7893/S	900	900	10000	210	0.23	0.0048

Sensitivity switch for the above gives: Direct, x 1, x 0.1, x 0.01, and Shorted positions, except for Cat. No. 7890/S which has Direct, x 0.1, x 0.01, x0.001, and Shorted positions. Cat. No. 7890/S fitted with special manual clamp. Sensitivity figures are for x 1 range except for 7890/S which is for Direct setting of shunt switch.

Model	Resistance (ohms)	Terminal resistance with shunt (ohms)	Critical damping resistance (ohms)	Typical sensitivity		
				(mm/μA)	(mm/μV)	(μA/mm)
7901/S	24	21.7	230	16	0.074	0.062
7902/S	110	102	1450	40	0.39	0.025
7903/S	420	396	7500	90	0.23	0.011
7904/S	1400	1320	25000	180	0.14	0.0056

Sensitivity switch for the above gives: Direct, x 1, x 0.05, x 0.01, x 0.001 and Shorted positions. The sensitivity figures given are in respect of the x 1 setting of the shunt switch.

Model	Resistance (ohms)	Terminal resistance with shunt (ohms)	Critical damping resistance (ohms)	Typical sensitivity		
				(mm/μA)	(mm/μV)	(μA/mm)
7901/T	24	21.7	230	32	1.47	0.031
7902/T	110	102	1450	80	0.78	0.012
7903/T	420	396	7500	180	0.45	0.0056
7904/T	1400	1320	25000	360	0.27	0.0028

Sensitivity switch for the above gives: Direct, x 1, x 0.05, x 0.01, x 0.001 and Shorted positions. The sensitivity figures given are in respect of the x 1 setting of the shunt switch.

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