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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 28, No. 4, April 1963

LEWIS ACID-BASE TITRATIONS EMPLOYING MEGACYCLE-FREQUENCY OSCILLATORS

II. TITRATION INVOLVING STANNIC CHLORIDE IN ACETONITRILE AND BENZENE SOLUTION

By using a megacycle-frequency oscillator to follow the reaction, the Lewis acid, stannic chloride, can be titrated with nitrogen bases in acetonitrile as solvent and with oxygen bases in benzene as solvent with an error of 0.5–4%; reverse-order titrations were equally successful.

The characteristic maxima and minima in the titration curves indicate that in acetonitrile stannic chloride probably forms AB, A_3B_4 and A_4B_3 adducts with piperidine, and AB and A_4B_3 adducts with pyridine; no adduct was indicated for diphenylamine. In benzene solution, stannic chloride forms (*a*) AB_2 adducts with MeOH, EtOH, *n*-PrOH, iso-PrOH, *n*-BuOH, *sec.*-BuOH and iso-BuOH, (*b*) AB and AB_2 adducts with acetone and tetrahydrofuran, and (*c*) an AB adduct with dioxane; the stoichiometry for a group of ethers is less decisive. The presence of the 1 : 1 tetrahydrofuran–stannic chloride adduct in benzene supports the belief that pentacoordinate tin exists in certain adducts with oxygen bases.

The megacycle-frequency oscillator was also applied to the estimation of the relative base strength of Lewis bases toward a given Lewis acid by assuming that the instrument response increase, as an ether or alcohol was added to stannic chloride in benzene, is due to the formation of the new coordinate bond. Agreement of the data obtained with the limited existing data on relative base strengths of ethers is good in those cases where comparable steric factors are involved.

E. T. HITCHCOCK AND P. J. ELVING, *Anal. Chim. Acta*, 28 (1963) 301–315

POTENTIOMETRIC TITRATION OF HYDROGEN PEROXIDE WITH AN ELECTROPOLISHED STAINLESS STEEL ELECTRODE

The preparation and use of a stainless steel indicator electrode in the accurate potentiometric titration of aqueous hydrogen peroxide are described. The results agree excellently with those obtained by a standard colorimetric weight-titration procedure. The nature of the titration curves, potential changes and the factors affecting them are discussed. Rapid potentiometric titrations directly to the equivalence-point potential are possible, owing to the nature of the titration curve.

P. SMITH, M. BISWAS AND W. C. VOSBURGH, *Anal. Chim. Acta*, 28 (1963) 316–322

DETERMINATION OF ORGANIC PERACIDS AND HYDROGEN PEROXIDE IN MIXTURES

A simple method for the determination of organic peracids and hydrogen peroxide in mixtures is presented. The method is based on the instantaneous reaction of peracids with neutral potassium iodide and on the formation of a stable complex between hydrogen peroxide and titanyl ions. This complex is decomposed with sodium fluoride and the ensuing reaction with iodide is accelerated with molybdic acid. The influence of the different additives on the analytical results has been studied.

T. LEDAAL AND E. BERNATEK, *Anal. Chim. Acta*, 28 (1963) 322–326

3,3′-DIHYDROXYBENZIDINE-N,N,N′,N′-TETRAACETIC ACID AS A METALLOFLUORESCENT INDICATOR IN EDTA TITRATIONS

3,3′-Dihydroxybenzidine-N,N,N′,N′-tetraacetic acid has been prepared and examined as a metallofluorescent indicator in compleximetric titrations. Copper(II) and lead(II) are determined by titration with EDTA in the presence of the indicator, the blue fluorescence of which is restored at the end-point. Manganese, zinc, cobalt and cadmium can also be determined if a dyestuff such as Rhodamine B is present along with the indicator.

G. F. Kirkbright and W. I. Stephen, *Anal. Chim. Acta*, 28 (1963) 327–330

ELIMINATION OF PHOSPHATE INTERFERENCE IN FLAME PHOTOMETRIC DETERMINATION OF STRONTIUM AND BARIUM

The interference of phosphate in the flame emission of calcium, strontium and barium was studied. The emission intensity decreases proportionally to the amount of interfering anion up to a maximum depression for equimolar amounts of phosphate to metal. A thermostable phosphate is formed before the cation enters the flame. Appropriate addition of lanthanum restores the three alkaline earth lines to their intensities in absence of phosphate, the lanthanum displacing the alkaline earths from their phosphates before the hot region of the flame is reached.

J. Yofé, R. Avni and M. Stiller, *Anal. Chim. Acta*, 28 (1963) 331–335

THE USE OF THE METHOD OF CONTINUOUS VARIATION FOR THE CLASSIFICATION OF COMPLEXES WITH MOLE RATIO 1 : 1

It is shown theoretically and experimentally that curves of continuous variation may be used to classify complexes of the form A_mB_n for which $m/n = 1$, into two different groups: one group comprises complexes for which $m = n = 1$, and another group contains those for which $m = n > 1$.

The system iron(III)–chrome azurol S was used to demonstrate the applicability of the method.

K. S. Klausen and F. J. Langmyhr, *Anal. Chim. Acta*, 28 (1963) 335–340

THE USE OF IMPREGNATED FILTERS TO COLLECT TRACES OF GASES IN THE ATMOSPHERE

II. COLLECTION OF SULFUR DIOXIDE ON MEMBRANE FILTERS

HA and AA Millipore filters impregnated with 5% potassium bicarbonate and dried were found to be suitable for sampling concentrations of sulfur dioxide in air. The impregnation technique and filter loadings are described; flow rates are relatively unaffected by impregnation. The apparatus and procedures used for preparation and sampling known concentrations of sulfur dioxide in air are described. Comparisons of actual and theoretical concentrations in the 0.1 to 10 p.p.m. range showed that the concentrations prepared must be assayed.

The collection efficiency of impregnated filters was evaluated for sodium tetrachloromercurate(II) (less than 10% which is in contrast with the 100% efficiency found with TCM as a scrubbing solution) and potassium bicarbonate (greater than 95%). The capacity of the filters was such that sampling a 10 p.p.m. sample for at least 1 h is possible.

J. B. Pate, J. P. Lodge, Jr. and M. P. Neary, *Anal. Chim. Acta*, 28 (1963) 341–348

THE SAMPLING OF SULFUR DIOXIDE IN AIR WITH IMPREGNATED FILTER PAPER

A method is suggested for the sampling of sulfur dioxide in air with impregnated filter paper instead of bubblers. The best aqueous impregnating solution contained potassium hydroxide with glycerol or triethanolamine. The possibilities and limitations of the method are discussed. High collection efficiencies (over 95%) were obtained at relative humidities above 25%. Collected sulfur dioxide was stable for at least several weeks when the filters were kept dry after the sampling. The method is especially suited for short-time measurements and for automatic sampling with smoke samplers.

C. Huygen, *Anal. Chim. Acta*, 28 (1963) 349–360

POLAROGRAPHY OF URANIUM IN LACTATE MEDIUM

The polarography of uranium(VI) in the lactate medium is studied at different pH values. At pH 1 the half-wave potential of the uranium(VI) wave remains the same as that of the simple ion, but the limiting current increases with increasing concentration of lactate; disproportionation of uranium(V) at the electrode surface is suggested. The rate of disproportionation is calculated.

Polarograms observed in the region of pH 5 and 6 are interpreted on the basis of complexation of UO_2^{2+}.

S. C. Saraiya and A. K. Sundaram, *Anal. Chim. Acta*, 28 (1963) 360–365

ANALYTICAL APPLICATIONS OF INFRA-RED SPECTROSCOPY

The behaviour of the oxinates of niobium, tantalum and associated metals in the infra-red region was studied and a method developed for the determination of niobium and tantalum. Vanadium caused no interference, but other heavy metals, such as molybdenum, manganese and cobalt, which interfered were removed by preliminary treatment when the method was applied to the determination of niobium and tantalum in steels.

R. J. Magee and I. Martin, *Anal. Chim. Acta*, 28 (1962) 366–370

ANION-EXCHANGE SEPARATION OF HYDROXY ACIDS IN ACETATE MEDIUM

A great number of hydroxy acids have been separated in an anion-exchange column using sodium acetate as eluant. It is essential that lactones be saponified before loading the column. With hydroxy acids containing only one or two hydroxyl groups this method is superior to separations in borate medium. With complicated mixtures the methods supplement each other.

B. Alfredsson, S. Bergdahl and O. Samuelson, *Anal. Chim. Acta*, 28 (1963) 371–377

THE SEPARATION OF Lu ,Yb AND Tm ON CATION-EXCHANGE RESIN WITH α-IHBA AS ELUANT

(in French)

The mutual separation of Lu, Yb and Tm is examined with cation-exchange resin and 0.1 *M* α-hydroxybutyric acid as eluant. When carrier amounts of *ca.* 1 mg of rare earths are eluted, the distribution constants are displaced and the elution peaks are asymmetrical. Quantitative separation is, however, possible at room temperature; separation requires 23 h at pH 3.83 but only 13 h with a pH gradient.

D. L. Massart et J. Hoste, *Anal. Chim. Acta*, 28 (1963) 378–382

SPECTROPHOTOMETRIC DETERMINATION OF BROMATE WITH *o*-ARSANILIC ACID

o-Arsanilic acid reacts with bromate ions in dilute acid solution and forms a reddish-brown color which is suitable for the spectrophotometric determination of bromate. The reaction has a sensitivity of 0.05 μg BrO_3^- per cm^2 for log $I_0/I = 0.001$ and obeys Beer's law up to 50 p.p.m. The standard deviation for the color development (387 p.p.m. bromate) is 0.95%, and 0.52% in the determination of bromate in salt solutions.

Optimum analytical conditions for the reaction have been established and a procedure for the spectrophotometric determination of bromate is given.

J. C. MACDONALD AND J. H. YOE, *Anal. Chim. Acta*, 28 (1963) 383–387

SPECTROPHOTOMETRIC DETERMINATION OF RARE EARTH METALS WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

1-(2-Pyridylazo)-2-naphthol (PAN) reacts very sensitively with rare earth metals to form a deep red precipitate in alkaline solution; this can be extracted with ether, exept in the case of lanthanum, cerium and scandium. Absorption maxima occur at 530 and 560 mμ. Traces of rare earth metals may be determined in the presence of many foreign metals.

SH. SHIBATA, *Anal. Chim. Acta*, 28 (1963) 388–392

ATOMIC ABSORPTION SPECTROSCOPY OF ALUMINUM

(Short Communication)

F. B. DOWLING, C. L. CHAKRABARTI AND G. R. LYLES, *Anal. Chim. Acta*, 28 (1963) 392–394

THE SPECTROPHOTOMETRIC DETERMINATION OF SOME ORGANIC ACIDS WITH COPPER BENZIDINE

(Short Communication)

Z. D. DRAGANIĆ, *Anal. Chim. Acta*, 28 (1963) 394–397

ANALYTICAL APPLICATIONS OF THE REACTION OF HEXACYANOFERRATE(III) WITH ASCORBIC ACID

PART VI. DETERMINATION OF HYDRAZINE

(Short Communication)

L. ERDEY, G. SVEHLA AND L. KOLTAI, *Anal. Chim. Acta*, 28 (1963) 398–399

LEWIS ACID-BASE TITRATIONS EMPLOYING MEGACYCLE-FREQUENCY OSCILLATORS

PART II. TITRATION INVOLVING STANNIC CHLORIDE IN ACETONITRILE AND BENZENE SOLUTION

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(Received September 12th, 1962)

The objectives of the present investigation of the applicability of megacycle-frequency oscillators to the study of Lewis acid-base reactions and the investigation of the reaction of aluminum chloride with a group of nitrogen bases in the basic solvent acetonitrile (dielectric constant 36) have been described[1]. The present paper is concerned with the reaction of the Lewis acid, stannic chloride, with various Lewis bases in acetonitrile and in the inert solvent benzene (dielectric constant 2.3). Since benzene exhibits a weakly basic character (in the Lewis sense) toward Lewis acids as demonstrated by complexation with iodine[2], silver ion[3] and anhydrous aluminum halides[4], it is classed as an inert solvent only with some qualification. However, its low dielectric constant does indicate that ionic dissociation will not be favored in it. Moreover, since the solvent benzene represents only slight competition for the acid, it is possible to study a much wider range of weak bases in this solvent.

In contrast to aluminum chloride (subl. 177.8°), stannic chloride is a low-boiling liquid with a greater covalent character (m.p. $-33°$; b.p. 114.1°). While aluminum in monomeric aluminum chloride has an incomplete valence shell, the tin atom in stannic chloride has already attained the inert gas electronic configuration. On the basis of this difference in configuration, stannic chloride is expected to be a weaker Lewis acid than aluminum chloride; this has been verified experimentally[5,6]. However, unlike the case of aluminum chloride[1], titrations involving stannic chloride and nitrogen bases in acetonitrile gave no precipitate. Solutions of stannic chloride in acetonitrile were easily prepared and standardized, and remained stable indefinitely.

Solubility of stannic chloride in organic solvents. Owing to its covalent character, stannic chloride is readily soluble in inert solvents such as hydrocarbons and halohydrocarbons. Little, if any, reaction seems to occur between it and benzene, as evidenced by the very small megacycle-frequency response of benzene solutions of stannic chloride (ref.[1]: Fig. 3) and the very small integral heat of dilution for stannic chloride in benzene[7] (see, however, the subsequent discussion under BASE STRENGTH CHARACTERISTIC). The appreciable solubility of stannic chloride in oxygen- or nitrogen-containing solvents is due to the basic character of the latter. No increase in megacycle-

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frequency oscillator response occurs when stannic chloride is added to acetonitrile, in which it is readily soluble; this is likely due to the already high response to the solvent alone, which "drowns out" the response to the stannic chloride–acetonitrile reaction. Evidence for the reaction can be noted, however, by comparing the curves of Fig. 1.

Conductivity studies indicate only a slight ionization of stannic chloride in thionyl chloride[8,9]. No evidence for dimerization in any solvent could be found.

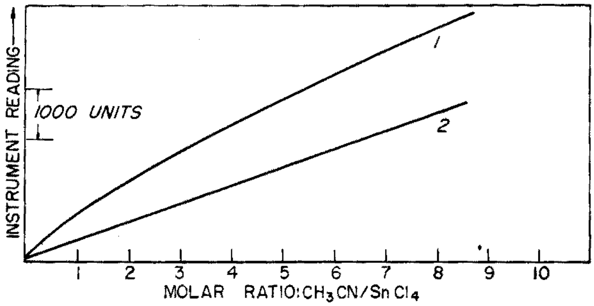


Fig. 1. Oscillator response on addition of acetonitrile to (*1*) 5.06 mmoles $SnCl_4$ in 100 ml of benzene and (*2*) 100 ml of benzene alone. Compensator setting: 1500.

BEHAVIOR IN ACETONITRILE SOLUTION

Table I summarizes the titration of nitrogen bases with stannic chloride; Fig. 2 gives typical titration curves. Unexpected were the definite inflections at molar ratios of approximately A_3B_4 and A_4B_3 for piperidine and A_4B_3 for pyridine; while these results are difficult to explain, they were none the less reproducible. Upon the addition of stannic chloride to diphenylamine, the instrument response increased continuously, leveling off at a molar ratio of about 1 : 5.

TABLE I

TITRATION OF NITROGEN BASES WITH STANNIC CHLORIDE IN ACETONITRILE

Base present		*Volume 0.0919 M $SnCl_4$ used*		*Molar ratio of base : $SnCl_4$*	
Amount taken (mmoles)	*Cell concn. (mM)*	*Break-1 (ml)*	*Break-2 (ml)*	*Break-1*	*Break-2*
		Piperidine			
0.0505	0.505	0.42	0.70	1.31	0.79
0.101	1.01	0.81	1.42	1.36	0.77
0.101	1.01	0.82	1.40	1.34	0.78
0.152	1.52	1.20	2.11	1.36	0.78
		Pyridine			
0.0557	0.557	0.76		0.80	
0.1115	1.115	1.50		0.81	

Table II summarizes the data for the reverse-order titrations, *i.e.*, acid added to base; Fig. 3 gives typical titration curves. While both piperidine and pyridine gave

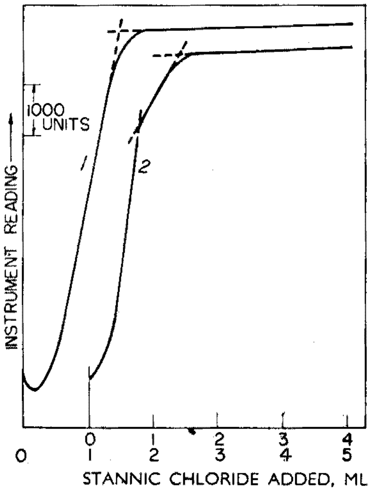


Fig. 2. Titration of 100 ml of nitrogen base solution with 0.0919 *M* $SnCl_4$: (*1*) 0.1115 mmole pyridine present; (*2*) 0.101 mmole piperidine. Solvent: acetonitrile; compensator setting: 0.

TABLE II

TITRATION OF STANNIC CHLORIDE WITH NITROGEN BASES IN ACETONITRILE

$SnCl_4$ present		*Molar ratio of Base : $SnCl_4$ at curve*	
Amount taken (mmoles)	*Cell concn. (mM)*	*Maximum*	*Minimum*
	Piperidine		
0.0459	0.459	1.16	2.87
0.0919	0.919	1.10	3.11
0.0919	0.919	1.08	3.43
	Pyridine		
0.0919	0.919	1.07	
0.1838	1.838	0.97	

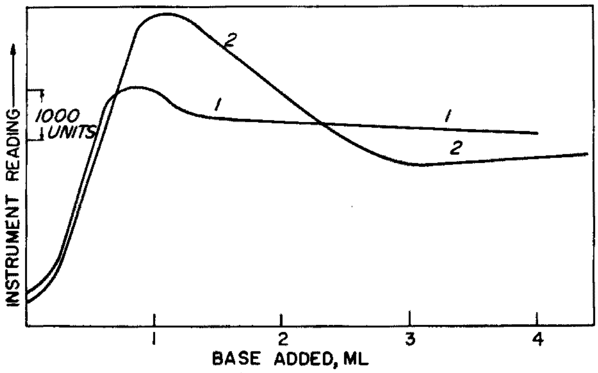


Fig. 3. Titration of 100 ml of 0.000919 *M* $SnCl_4$ solution with (*1*) 0.1115 *M* pyridine and (*2*) 0.101 *M* piperidine. Solvent: acetonitrile; compensator setting: 0.

maxima at very close to a 1 : 1 molar ratio, neither gave definite minima, *e.g.*, the minima in the piperidine curves varied in three titrations between molar ratios of 2.7 and 3.4. In the case of pyridine the titration curve dropped immediately following the maximum and then continued in a straight line with slight negative slope. The curve for diphenylamine addition was very similar in shape to that for the reverse-order titration; no characteristic inflection was seen.

BEHAVIOR IN BENZENE SOLUTION

The megacycle-frequency oscillator response to reactions between Lewis acids and bases in a very low dielectric constant medium such as benzene, in which ionization is not expected to occur, should be due primarily to the polar character of the donor-acceptor species formed, if the latter adduct is soluble in the solvent. Because of the very low instrument response to benzene itself, the instrument sensitivity may be greatly increased by the addition of series inductance[1], permitting detection of the formation of such weak coordinate bonds as those in stannic chloride–ether com-

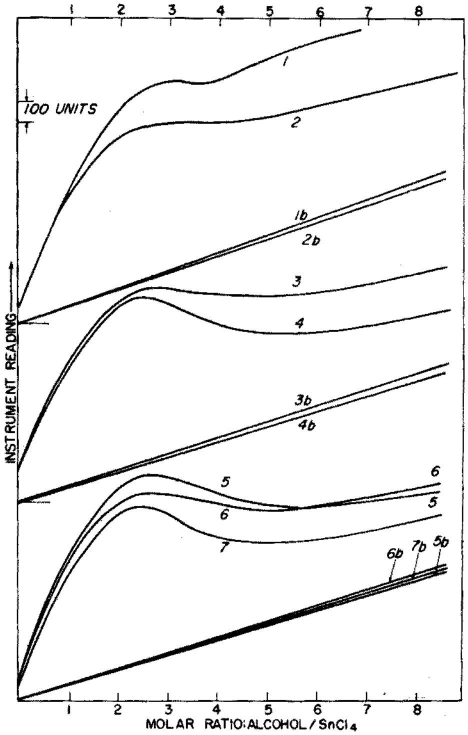


Fig. 4. Oscillator response on addition of pure alcohol to (*a*) 5.0 mmoles $SnCl_4$ in 100 ml of benzene (curves marked only with numerals) and (*b*) 100 ml of benzene alone (curves also marked with *b*). Compensator setting: 1500. 1 = methyl alcohol; 2 = ethyl alcohol; 3 = *n*-propyl alcohol; 4 = iso-propyl alcohol; 5 = iso-butyl alcohol; 6 = *n*-butyl alcohol; 7 = *sec.*-butyl alcohol.

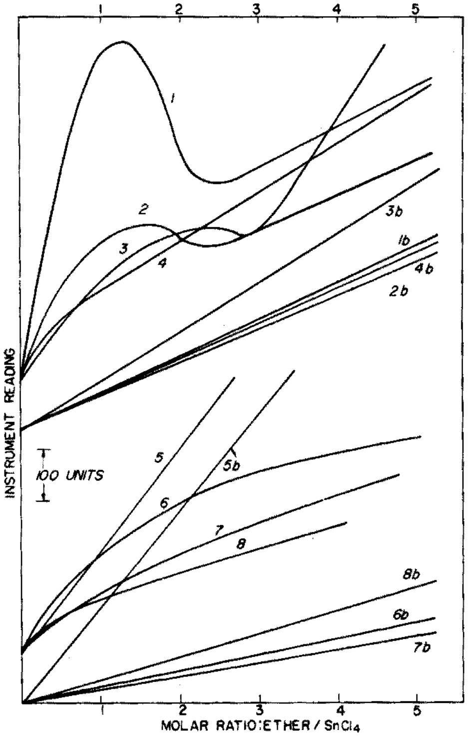


Fig. 5. Oscillator response on addition of pure ether to (*a*) 5.0 mmoles $SnCl_4$ in 100 ml of benzene (curves marked only with numerals) and (*b*) 100 ml of benzene alone (curves also marked with *b*). Compensator setting: 1500. 1 = tetrahydrofuran; 2 = tetrahydropyran; 3 = propylene oxide; 4 = cineole; 5 = bis(2-chloroethyl) ether; 6 = ethyl ether; 7 = *n*-butyl ether; 8 = iso-propyl ether.

plexes. A compensator setting of 1500 was used for all of the studies in benzene.

Titrations involving nitrogen bases. Titration of stannic chloride in benzene with pyridine, piperidine, *p*-toluidine and *n*-butylamine gave from the very beginning of the titration a precipitate which coated the cell walls and stirrer. The change in instrument response during titration was negligibly small with no significant inflection in the titration curve, suggesting that the adducts are highly insoluble. Addition of acetonitrile gave a positive response without a precipitate (Fig. 1).

Titrations involving oxygen bases. The reaction between 0.05 *M* stannic chloride in benzene and oxygen bases such as alcohols, ethers, ketones and esters gave soluble products (with the exception of *tert.*-butyl alcohol and *p*-dioxane); the instrument response was related to the type and concentration of soluble complex formed.

All titration curves (Fig. 4) for the addition of pure alcohols (methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, *sec.*-butyl and iso-butyl) to stannic chloride show a maximum at the AB_2 molar ratio, followed by a broad minimum; finally, the curve runs parallel to the concentration response curve for the alcohol. The position of the minimum differs for each alcohol, ranging from a molar ratio of about $AB_{3.5}$ for methyl alcohol to AB_5 for the propyl alcohols. No definite interpretation regarding stoichiometry seems possible from the minima, but the maxima, all at exactly AB_2 molar ratio, indicate the formation of stable adducts of this composition.

In general, the curves obtained (Fig. 5) when cyclic ethers (tetrahydrofuran (THF), tetrahydropyran and propylene oxide) are added to stannic chloride, show a maximum, then decrease to a minimum, and finally increase in a straight line parallel to the concentration response curve for the ether involved. The general shape of the curve parallels that found for the low-frequency conductance titration of

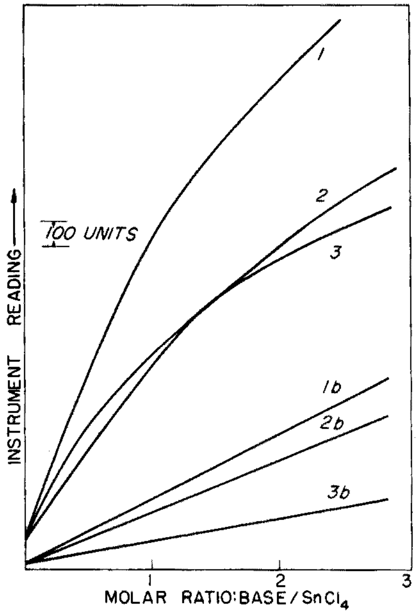


Fig. 6. Oscillator response on addition of pure oxygen base to (*a*) 5.0 mmoles $SnCl_4$ in 100 ml of benzene (curves marked only with numerals) and (*b*) 100 ml of benzene alone (curves also marked with *b*). Compensator setting: 1500. 1 = cyclohexanone; 2 = acetone; 3 = ethyl acetate.

stannic chloride with THF, in which the final increasing segment of the curve was ascribed to an ion-pair species, $(THF)_3SnCl_3^+$, Cl^-, formed by the excess base[10].

Noncyclic ethers (ethyl, bis(2-chloroethyl), iso-propyl and *n*-propyl), cineole, ketones (cyclohexanone and acetone), and ethyl acetate (Figs. 5 and 6) give a steadily increasing curve on addition to stannic chloride, which finally approaches a straight line similar to the concentration response curve of the oxygen base. While the positions of inflections do not indicate conclusively in all cases any definite stoichiometry, the magnitude of the response at the 1 : 1 molar ratio, for the ethers at least, is directly related to the base strength of the ether with respect to the stannic chloride molecule (*cf.* subsequent discussion).

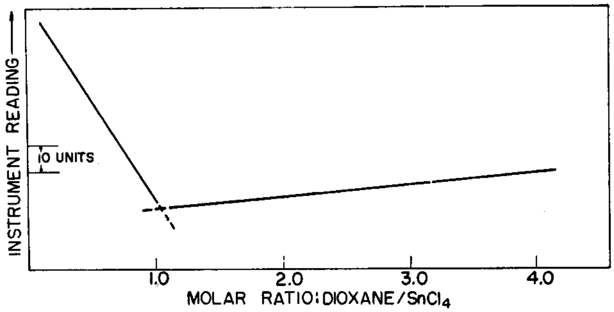


Fig. 7. Oscillator response on addition of pure *p*-dioxane to 5.0 mmoles $SnCl_4$ in 100 ml of benzene. Compensator setting: 1500.

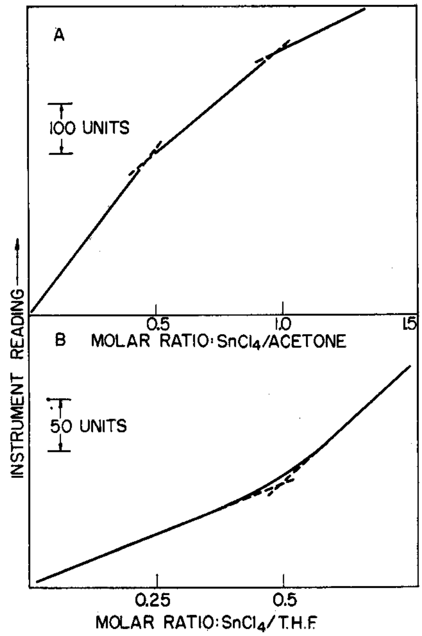


Fig. 8. Oscillator response on addition of 0.2025 *M* $SnCl_4$ to 100 ml of solution containing (*A*) 3.4 mmoles acetone and (*B*) 2.03 mmoles tetrahydrofuran. Solvent: benzene; compensator setting: 1500.

The addition of *p*-dioxane (Fig. 7) produces an immediate precipitate; the instrument response decreases linearly until the 1 : 1 molar ratio is reached and then increases parallel to the straight-line concentration-response curve for *p*-dioxane, indicating that, after the stannic chloride has been precipitated, the response is only due to the increasing *p*-dioxane concentration. The molar ratio of AB is in conformity with the behavior of dioxane as a diacid Lewis base[9]. The formation of a 1 : 1 stannic chloride–dioxane adduct has been ascribed to chelation with the dioxane being involved in a bidentate linkage with the tin, which would require conversion of the dioxane from its normal Z-form to a U-form (*cf.* ref.[10]). It seems more probable that the adduct is of a more or less polymeric nature in which each dioxane molecule acts as a connecting link between two stannic chloride molecules. Polymer formation is supported by insolubility of the adduct, whereas a chelate complex would not be likely to be insoluble in benzene.

The instrument response increases continuously upon addition of 0.2 *M* stannic chloride to a benzene solution of each of the following oxygen bases: Et_2O, iso-Pr_2O, THF, acetone and methyl ethyl ketone. However, significant inflections are seen only in the THF and acetone titration curves (Fig. 8), corresponding to formation of the AB_2 complex for THF (no break is detected at the 1 : 1 ratio) and at both the AB and AB_2 molar ratios for acetone. The titration of THF–acetone mixtures did not prove satisfactory for differentiating between the two bases. Addition of stannic chloride to *p*-dioxane in benzene gave no significant change in instrument response even when a fivefold excess was added.

ISOLATION OF A BASE STRENGTH CHARACTERISTIC

Basis of the approach. The use of a compensator, *i.e.*, addition of series inductance, in connection with the oscillator has been discussed[1]. No series inductance was used for the studies in acetonitrile, but a setting of 1500 units was used for those in benzene. At this setting, the instrument response is linear with the dielectric constant of the cell contents (as long as there is no conductivity) for both the large cell used in the present work and the small cell which is also available; similar linearity has been observed by others[11]. The use of a high compensator setting also increases the sensitivity of instrument response.

Since the oscillator response varies linearly with the dielectric constant of the cell contents for nonconducting solutions and with the concentration of a polar compound in such solutions, it may be assumed to a first approximation that the change in instrument response on titration of stannic chloride with a series of Lewis bases in benzene is due to formation of the coordinate covalent linkage of the adduct, and that all other factors in titrating a series of compounds essentially cancel. Consequently, one may represent the instrument response, *R*, for the Lewis acid-base reaction

$$A + :B \rightarrow A:B \qquad (1)$$

as

$$R = f(P_A C_{At}, P_B C_{Bt}, P_{\text{bond}} C_x) + R_{\text{solvent}} \qquad (2)$$

where P_A and P_B are the polarizabilities, and C_{At} and C_{Bt} the total concentrations of A and B in solution, and P_{bond} is the polarizability of the polar bond and C_x its concentration (*cf.* ref.[12] for detailed derivation).

In equation 2, $f(P_{\text{bond}} C_x)$ may be termed "bond response", R_{bond}, and may be considered to be represented by the change in instrument response due to formation of the coordinate bond at concentration C_x. This response should be primarily a relative measure of the polarity of the coordinate bond formed and therefore a relative measure of the base strength (electron donor tendency) of a given Lewis base with respect to a given Lewis acid. Solving equation 2, for "bond response",

$$\begin{aligned} R_{\text{bond}} &= \mathrm{f}(P_{\text{bond}}\, C_x) = R - \mathrm{f}(P_A C_{At},\, P_B C_{Bt}) - R_{\text{solvent}} \\ &= R - R_A - R_B - R_{\text{solvent}} \end{aligned} \qquad (3)$$

where R_A and R_B are the experimentally determined instrument responses to free A and B, respectively, at concentration C_x.

A typical experimental situation is shown in Fig. 9. Line AB is the concentration response for the Lewis base; distance AC corresponds to the response due to the addition of a given amount of Lewis acid to the solvent alone (making concentration C_x); CE is the response obtained upon continuous addition of base to the acid solution. At the 1 : 1 molar ratio, *ab*, *bc*, *cd* and *de* are the respective responses of the solvent, R, the base added, R_B, the acid added, R_A, and the "bond response", R_{bond}. Solving for "bond response",

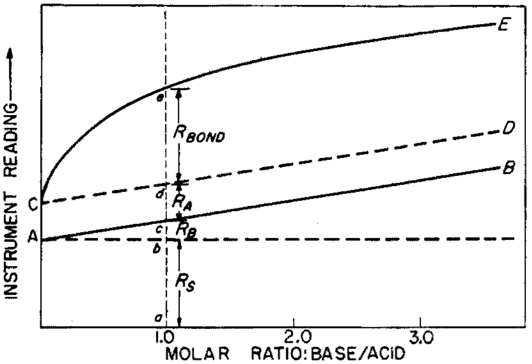


Fig. 9. Analysis for "bond response", R_{bond}, of a hypothetical megacycle-frequency oscillator response curve for Lewis acid-base interaction in an inert solvent. The distance *ab* corresponds to the response due to solvent alone, *bc* and *cd* to the responses due to presence of base and acid, respectively, at a given concentration (molar ratio = 1 : 1), and *de* to the response due to interaction of the base with the acid at the given concentration.

$$R_{\text{bond}} = de = ae - ad \qquad (4)$$

Assuming that the "bond response" is a measure of the base strength of B with respect to A, a simple and rapid method of comparing base strengths relative to a given Lewis acid is thus available.

In the present derivation, no allowance has been made for interaction between components and solvent. Although inert solvents such as benzene are quite unreactive, there is evidence that some slight association does occur between benzene and stannic chloride based on the instrument response observed in this study, when stannic chloride is added to benzene. The response is much greater than would be predicted from the dielectric constant of pure stannic chloride (2.87), *e.g.*, the difference in response between 100 ml of 0.05 M stannic chloride in benzene and 100 ml of pure benzene is approximately 100 instrument units, while the increase in response due to the presence of an equal amount of diethyl ether (dielectric constant 4.33) in benzene is only 26 units. Such a result is not surprising; it merely verifies the belief that benzene can behave as a Lewis base and coordinate with an acid[2,3,13]. Addition of a base which is considerably stronger than benzene, is likely to cause a partial displacement of solvent with a corresponding decrease in the response due to the Lewis acid–solvent association. It can not be assumed, however, that this contribution falls to zero. Since it was not known how much to allow for the decrease in acid–solvent response, the full 100 instrument units were used in the present study as the response due to the 0.05 *M* stannic chloride in benzene regardless of the oxygen base added. Since this procedure was used in every case, the relative values obtained for the basicities of the various oxygen bases should not be greatly affected. (The ultraviolet absorption observed when stannic chloride is dissolved in toluene has been considered as due to a charge transfer process of the type described by Mulliken[3].)

Correlation with other base strength measurements. The megacycle-frequency "bond response", R_{bond}, at 1 : 1 molar ratios and at a concentration of 0.05 *M*, for the complexes formed between stannic chloride and the series of oxygen bases investigated are compared in Table III and Fig. 10 with the data obtained for these compounds by other methods for measuring relative base strength.

No relationship is seen to exist between dielectric constant and base strength, a fact which has been previously noted[14,15].

The lack of good correlation between "bond response" and heat of mixing[16] is

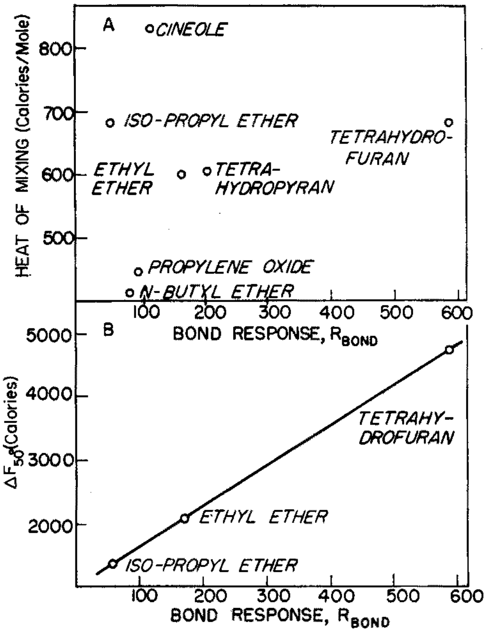


Fig. 10. Correlation of the megacycle-frequency oscillator response in instrument units due to interaction of $SnCl_4$ and ethers in benzene (both 0.05 *M*) with other base strength data for ethers: (*A*) heat of mixing with chloroform (calories/mole)[16]; (*B*) molar free energy of dissociation for the complex $R_2O : BF_3$[17].

TABLE III

RELATIVE BASE STRENGTH OF OXYGEN BASES AS MEASURED BY VARIOUS TECHNIQUES

Oxygen base	Dielectric constant	"Bond response"[a]	Megacycle-frequency oscillator: Position of curve maximum — Ratio	Megacycle-frequency oscillator: Position of curve maximum — Units	Methanol O-D shift[b] (cm^{-1})	Heat of mixing[c] (cal/mole)	P.M.R. value[d]	$\Delta F 50°$ $R_2O : BF_3$[e] (kcal/mole)
			Ethers					
Tetrahydrofuran	7.59	584	1.20	586	117	677	0.17	4660
Tetrahydropyran	—	206	1.56	207	115	600	0.16	—
Ethyl ether	4.33	168	—	—	96	597	—	2020
Cineole	4.57	112	—	—	125	835	—	—
Propylene oxide	—	100	2.35	170	99	443	—	—
n-Butyl ether	3.06	87	—	—	101	412	—	—
iso-Propyl ether	3.88	57	—	—	110	678	—	1340
bis(2-Chloroethyl) ether	21.2	18	—	—	—	—	—	—
Dioxane	2.21	pptn.	—	—	—	—	—	—
Dioxolane	—	320	—	—	—	—	—	—
			Alcohols					
Methyl alcohol	32.63	470	2.00	925	—	—	0.01	—
Ethyl alcohol	24.30	450	1.96	730	—	—	0.05	—
n-Propyl alcohol	20.1	520	2.03	850	—	—	0.05	—
iso-Propyl alcohol	18.3	490	2.05	830	—	—	0.01	—
n-Butyl alcohol	17.1	485	1.96	810	—	—	0.00	—
iso-Butyl alcohol	17.7	515	2.08	930	—	—	0.02	—
sec.-Butyl alcohol	15.8	460	2.08	750	—	—	0.03	—
			Ketones					
Acetone	20.7	470	—	—	—	—	—	—
Cyclohexanone	18.3	920	—	—	—	—	—	—
Ethyl acetate	6.02	625	—	—	—	—	—	—

[a] Response of megacycle-frequency oscillator circuit, in oscillometer units, at the 1 : 1 molar ratio (base/$SnCl_4$) and a concentration of 0.0528 *M* in the adduct.

[b] Shift of the O-D band in the infrared spectrum of methanol-d for 1.0 *M* methanol-d in the various ethers. The reference solvent was carbon tetrachloride[16].

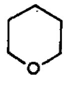
[c] Heat of mixing when one mole of ether is mixed with one mole of chloroform at 25°[16].

[d] Proton magnetic resonance δ values for the αCH_2 in the cyclic ether[34] and the OH proton in the alcohols[35].

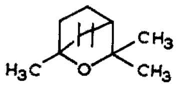
[e] Free energy of dissociation at 50° for the reaction[17]: $R_2O : BF_3 \rightleftharpoons R_2O : + BF_3$.

believed to be primarily due to the difference in steric nature of the two reactions being compared. For heat of mixing, the reaction involves hydrogen bonding of the chloroform hydrogen to the ether donor oxygen; the reaction in the present study involves a much larger acceptor, the stannic chloride molecule. (It must be remembered that stannic chloride is a relatively large molecule compared to the Lewis acids used in some of the reported studies on base strength.) The effects of the steric factors discussed by **Brown** *et al.*[17–20] are significant to the present comparison and may well account for some or all of the deviation from linearity in Fig. 10A. In general, the orders of base strength for the seven ethers agree except for iso-propyl ether and cineole.

Cineole may be considered a methyl-substituted tetrahydropyran with a dimethylene bridge between carbon atoms 2 and 5:



Tetrahydropyran



Cineole

Owing to the inductive effect of the methyl groups, the oxygen in cineole should have a greater electron density than the oxygen in tetrahydropyran and, consequently, greater intrinsic base strength. This is verified by the greater molar heat of mixing with chloroform. However, the apparent reverse order of basicity with respect to stannic chloride likely results from steric hindrance to the approach of the large stannic chloride molecule to the cineole oxygen; the steric strain involved in forming the complex is more effective than the increased electron density of the donor oxygen; this type of strain is virtually nonexistent in hydrogen-bonding reactions because of the small size of the hydrogen atom.

It is apparent from Fisher-Hirschfelder-Taylor models of the ethers that the greater shielding of the donor oxygen by neighboring methyl groups in cineole and iso-propyl ether would hinder the approach of the relatively large stannic chloride molecule and thus decrease the apparent base strength of these ethers with respect to stannic chloride. The reversal in base strength of ethyl ether and iso-propyl ether is thus explicable.

When the steric effects are comparable, differences in inductive effect will be evident, *e.g.*, ethyl ether is more basic with respect to stannic chloride than bis(2-chloroethyl) ether as expected on the basis of the inductive effect alone.

The correlation of "bond response" with the free energy of dissociation for the complexes formed in the reaction of ethers with BF_3[17] is very good (Fig. 10B). This reaction should more closely parallel the stannic chloride–ether interaction with regard to steric factors, since the two Lewis acids are comparable in size.

Reported measurements on relative base strengths of alcohols are relatively rare, probably owing to their self-association in the liquid state, which complicates the interpretation of data on experiments involving the liquid alcohols. However, the effect of self-association should be less pronounced at high dilution in an inert solvent; consequently, the results obtained by the present technique should not be seriously affected by self-association.

DISCUSSION

The present studies, of which this is the second, have explored the utility of megacycle-frequency oscillators for following Lewis acid-base reactions in solution from the viewpoints of (*a*) the quantitative titrimetric determination of Lewis acids and bases, (*b*) the evaluation of the stoichiometry of their reactions, and (*c*) the measurement of relative base strength of Lewis bases with respect to a given Lewis acid.

The titrimetric and stoichiometric problems have been examined in this and the previous paper[1]. Titration of stannic chloride with Lewis bases in oxychlorides of phosphorus, sulfur and selenium, benzene and other solvents, using thermometric, cryoscopic, conductometric, potentiometric and indicator end-point determination has been described[7,8,10,15,21-25]. In the present study, nitrogen bases in acetonitrile as solvent have been successfully titrated with the Lewis acids, aluminum chloride and stannic chloride, with an error in accuracy ranging from 0.5 to 4%; reverse-order titrations are equally successful. Reaction of stannic chloride with oxygen bases such as tetrahydrofuran and dioxane in benzene solution permit titrations of comparable accuracy. While the latter accuracy is considerably less than that possible in conventional protonic acid-base titrations in aqueous and nonaqueous media, it compares favorably with that attainable with other techniques used to follow Lewis acid-base reactions in solution. An added advantage is that the characteristic response of the megacycle-frequency oscillator circuit to coordinate bond formation in inert solvents permits reactions to be followed even when solution conductivity is virtually nil.

The characteristic shapes of the titration curves obtained (positions of maxima, minima and other inflections) give information regarding the species forming during the course of the reaction. The information thus obtained on the stoichiometry of the stannic chloride adducts with Lewis bases is subsequently discussed.

In addition, the megacycle-frequency oscillator may be applicable to the study of the relative base strengths of weak bases toward Lewis acids. Introduction of appropriate series inductance into the oscillator circuit makes the instrument response linear to the dielectric constant of the cell contents. As an ether is added to stannic chloride in benzene, the instrument response increases owing to the formation of the new coordinate bond. When the molar ratio is 1 : 1, the response is considered to be directly related to the polarity of the coordinate bond formed and therefore a measure of the base strength of the ether with respect to stannic chloride. Consequently, by analysis of their titration curves, a series of ethers have been arranged in order of base strength toward stannic chloride in benzene as solvent. Agreement of these data with the limited existing data on relative base strength is quite satisfactory when comparable steric factors are involved.

Complexation of stannic chloride with nitrogen and oxygen bases. Addition of compounds possessing sufficiently strong donor groups to stannic chloride (pure or in solution) causes a reaction, in which tin usually increases its coordination number to six[8,24,26-30].

Unlike the transitional elements showing a coordination number of six, the tin atom already has its underlying *d*-orbitals filled. When tin exhibits a coordination number greater than four, the *d*-orbitals of the valence shell of tin must be utilized[31]. If the outer *d*-orbitals are used, the coordination number of six must be attained through sp^3d^2 hybridization, giving the symmetrical octahedral configuration with the valence bonds directed toward the six corners of a regular octahedron. The formation of 2 : 1 adducts between alcohols and stannic chloride in benzene is clearly evident from their titration curves.

Formation of stannic chloride complexes, in which the ligand : $SnCl_4$ ratio is different from 2 : 1, has been reported[24,26,27]. Usually it can be shown either that such complexes ionize or that the solvent becomes involved in the complex and, consequently, the coordination number of six is still maintained for tin, *e.g.*, stannic chloride trihydrate[26], $[SnCl_3 \cdot (H_2O)_3]^+ Cl^-$ or $[H_2O \cdot SnCl_4 \cdot OH]^- H_3O^+$, and the 1 : 1 triethylamine–stannic chloride complex in thionyl chloride[24], $[(C_2H_5)_3NSOCl] \cdot SOCl \cdot SnCl_6$.

Formation in acetonitrile of 1 : 1 complexes between stannic chloride and nitrogen bases is indicated in the present investigation since maxima occur in the megacycle-frequency titration curves at this ratio. The complexes likely contain a solvent molecule as a second added ligand, thus giving tin a coordination number of 6.

In benzene, formation of a 1 : 1 complex with stannic chloride seems to be indicated for some of the ethers studied. Since benzene is not expected to take part in the complexation, the possibility of pentacoordinate tin in these complexes has to be considered. Such complexes would involve sp^3d hybridization of the tin orbitals giving a bipyramidal configuration. While such configurations are rare, other experimental evidence points to this configuration for certain tin complexes, *e.g.*, WOOLF[32] has prepared 1 : 1 complexes of stannic fluoride with trimethylamine, dioxane and tetrahydrofuran, and LAUBENGAYER AND SMITH[29] have shown that the 2 : 1 ethanol–stannic chloride adduct splits off hydrogen chloride giving $(C_2H_5OH)(C_2H_5O)SnCl_3$, which may involve pentacoordinate tin.

The preparation and characterization of solid adducts of stannic chloride and various oxygen bases will be described in a subsequent paper[33].

EXPERIMENTAL

General experimental details have been described[1].

Chemicals

Stannic chloride solutions, 0.1 *M* in acetonitrile and 0.2 *M* in benzene, were prepared by pipetting the necessary amount of anhydrous $SnCl_4$ into the anhydrous solvent and then standardized by adding a 2.0-ml aliquot to 50 ml of methyl alcohol and 1.0 ml of 5 *M* nitric acid, and titrating the chloride potentiometrically with 0.1 *M* silver nitrate. The benzene solution was stored in automatic burets equipped with drying tubes.

The following reagent-grade ethers were purified by refluxing with lithium aluminum hydride and distilling through a 24-inch Fenske column: ethyl ether, iso-propyl ether, *n*-butyl ether, bis(2-chloroethyl) ether, tetrahydrofuran and tetrahydropyran. Dioxane (Eastman Kodak white label) and cineole (yellow label) were distilled from sodium metal through the same column. Purified propylene oxide was kindly supplied by Sister Mary Brandon Hudson. All ethers were distilled out of contact with air and were stored under nitrogen in glass-stoppered bottles in the dark at 7°; they were used only after a negative test for peroxide.

Titration procedures in benzene

Approximately 75 ml of anhydrous benzene was placed in the megacycle-frequency titration cell, followed by 25.00 ml of 0.2 *M* stannic chloride in benzene. The cell cap was quickly put in place, the flushing gas (nitrogen) allowed to flow into the upper space of the titration cell, and the stirrer started. After the initial instrument reading, the pure oxygen base was added in *ca.* 0.06 to 0.10-ml increments. Instrument-reading stability was attained in a matter of seconds, after which the reading was noted. The base was added until a molar ratio (base/$SnCl_4$) of about 5 : 1 was reached. No correction for dilution was applied to the instrument reading, since a total of not more than 2 or 3 ml of base was added.

In carrying out the reverse titrations (base with stannic chloride), much larger volumes of titrant were used, and the usual corrections for dilution were applied when necessary.

The authors wish to thank the U. S. Atomic Energy Commission, which helped support the work described. One author (E.T.H.) also wishes to thank the Standard Oil Company of Ohio for a fellowship.

SUMMARY

By using a megacycle-frequency oscillator to follow the reaction, the Lewis acid, stannic chloride, can be titrated with nitrogen bases in acetonitrile as solvent and with oxygen bases in benzene as solvent with an error of 0.5–4%; reverse-order titrations were equally successful.

The characteristic maxima and minima in the titration curves indicate that in acetonitrile stannic chloride probably forms AB, A_3B_4 and A_4B_8 adducts with piperidine, and AB and A_4B_3 adducts with pyridine; no adduct was indicated for diphenylamine. In benzene solution, stannic chloride forms (*a*) AB_2 adducts with MeOH, EtOH, *n*-PrOH, iso-PrOH, *n*-BuOH, *sec.*-BuOH and iso-BuOH, (*b*) AB and AB_2 adducts with acetone and tetrahydrofuran, and (*c*) an AB adduct with dioxane; the stoichiometry for a group of ethers is less decisive. The presence of the 1 : 1 tetrahydrofuran–stannic chloride adduct in benzene supports the belief that pentacoordinate tin exists in certain adducts with oxygen bases.

The megacycle-frequency oscillator was also applied to the estimation of the relative base strength of Lewis bases toward a given Lewis acid by assuming that the instrument response increase, as an ether or alcohol was added to stannic chloride in benzene, is due to the formation of the new coordinate bond. Agreement of the data obtained with the limited existing data on relative base strengths of ethers is good in those cases where comparable steric factors are involved.

RÉSUMÉ

Les auteurs ont effectué le titrage de l'acide de Lewis, $SnCl_4$, à l'aide de bases azotées, dans l'acétonitrile (comme solvant) et de bases oxygénées dans le benzène, en utilisant un oscillateur à fréquences de l'ordre du mégacycle. Un tel oscillateur a également été appliqué à la détermination de la force relative de bases de Lewis, par rapport à un acide de Lewis donné.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Titration von Lewissäure ($SnCl_4$) mit Stickstoffbasen und Sauerstoffbasen unter Verwendung eines Hochfrequenzoszillators. Das Verfahren eignet sich auch zur Feststellung der Basizität einer Lewisbase gegenüber einer gegebenen Lewissäure.

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POTENTIOMETRIC TITRATION OF HYDROGEN PEROXIDE WITH AN ELECTROPOLISHED STAINLESS STEEL ELECTRODE

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The potentiometric titration of aqueous hydrogen peroxide is usually carried out with platinum[1-6] or gold[7] indicator electrodes. To what extent the possible catalytic decomposition of aqueous hydrogen peroxide (0.01–0.1 *M*) by platinum[10-12] or gold[10,12] can affect the accuracy of these potentiometric titrations is not known. Stainless steel is less active than platinum or gold towards concentrated hydrogen peroxide[8,9]. The activity of stainless steel towards dilute aqueous hydrogen peroxide relative to platinum or gold might be different[8], but no data on this point are available. The aim of this investigation was to test whether stainless steel is a satisfactory electrode material for the potentiometric weight-titration of aqueous hydrogen peroxide. Stainless steel has the practical advantage over platinum and gold of being cheaper and more readily available.

The permanganate weight-titration procedure of HUCKABA AND KEYES[13] using the colorimetric method for the end-point determination is the standard method of determining hydrogen peroxide[8,13,14]. Consequently the procedure adopted was to compare the concentration of a solution of hydrogen peroxide as found by the method of HUCKABA AND KEYES[13] with that obtained using a potentiometric weight-titration procedure employing a stainless steel electrode.

EXPERIMENTAL

Apparatus

For the potentiometric titrations, the indicator electrode was a solid rod of stainless steel[8], AISI type 303, 17 cm long and 0.5 cm diameter, one portion of which (*ca.* 10 cm long from one end) was polished mechanically[15] first with five lots of emery paper of increasing fineness and then with rouge paper. Next it was rubbed clean with cotton soaked in purified[16] benzene[15] and electrolytically polished using UHLIG's method[15]. The polished electrode was pickled for 3–4 h in 50% (w/w) nitric acid[17], washed free of acid using distilled water followed by conductivity water, immersed in 1.5 *M* aqueous hydrogen peroxide[17] overnight and thoroughly washed with conductivity water before use. Between titrations it was kept immersed in 1.0 *M* aqueous sulphuric acid made up in conductivity water. The reference electrode was a mercury–mercurous sulphate half-cell with a 0.5 *M* sulphuric acid bridge[18]. Measurements were made with a Beckman Model G pH-meter. The titrations were carried out at

21–25° in a 250-ml beaker fitted with a mechanically driven glass-covered magnetic stirrer, a 60-ml capacity weight-buret being used.

All non-potentiometric titrations were conducted in a similar fashion except that the electrodes were omitted from the beaker.

Glassware

All glassware was Pyrex. Glassware coming into contact with hydrogen peroxide was steeped in warm dilute aqueous detergent solution and rinsed well with distilled water, then in a hot aqueous solution *ca.* 3 *M* in nitric acid and 0.5 *M* in hydrogen peroxide. After thorough washing in turn with distilled water, deionized water and lastly with conductivity water, it was steamed for at least 15 min, allowed to drain and then pumped dry in a high-vacuum line. Aqueous solutions of hydrogen peroxide are notoriously unstable unless very carefully handled[19–21]. The comparisons carried out in this work would have been much less successful without these precautions.

Materials

Deionized water was prepared from ordinary tap-distilled water using Amberlite MB-3 resin. Conductivity water was made by fractionally distilling deionized water in an all-Pyrex still in turn from acidic and alkaline aqueous potassium permanganate. This was high-quality water found suitable for kinetic studies of the photodecomposition of aqueous hydrogen peroxide[22]. All aqueous solutions used throughout this study were made with conductivity water unless otherwise stated. Steam was generated by boiling deionized water *ca.* 0.05 *M* in hydrogen peroxide.

Becco, nominally 98% (w/w), hydrogen peroxide was employed without further purification, except in one case when it was twice recrystallized before use, with no noticeable effect on the results (see Table I). It was handled and stored in subdued light wherever possible.

All other materials used were of reagent grade, the sodium oxalate (Thorn Smith, Michigan) having factor purity 100.19%. The standard solution of potassium permanganate was prepared with deionized water essentially by the method of HUCKABA AND KEYES[13]. It was standardized by weight-titration against sodium oxalate[13], following the procedure of FOWLER AND BRIGHT[23]. The concentration was 0.322% (w/w), corresponding to *ca.* 0.02 *M*.

Procedure

A stock solution of hydrogen peroxide was made up by weighing 1.5 g of the concentrated material into a 100-ml glass-stoppered volumetric flask, diluting to the mark with 0.02 *M* sulphuric acid solution in conductivity water and reweighing. The stock solution was stored in the dark at room temperature, 21–25°, and used without delay.

One such stock solution was titrated three times non-potentiometrically when fresh and again after 24 h with the following results, 97.639±0.031 and 97.648±0.039% (w/w), respectively, indicating no measurable concentration change. In another solution made up without the sulphuric acid, a 0.39±0.22% (w/w) concentration difference was observed after an interval of 24 h. Thus, addition of acid eliminated the possibility of any appreciable decomposition[24] of the stock solution during the 4–6 h for the six successive titrations necessary for each comparison (see below).

A sample of the stock solution was transferred to a 50-ml beaker and a 5-ml aliquot weighed into a weighing bottle, rinsed quantitatively with 100 ml of conductivity water (0.73 *M* in sulphuric acid) into a beaker, and weight-titrated with moderate stirring without using the electrodes. The rate of addition of the permanganate was 35–40 ml per min as recommended by HUCKABA AND KEYES[13]. The end-point was determined within a third of a drop[13] (*i.e.* 0.012–0.015 g) and the correction for excess color then applied[13]. Three successive colorimetric titrations were performed in this way. They were followed by three more titrations in which the procedure was essentially the same, save that near the end-point the electrodes were inserted and the course of the titration followed potentiometrically. The end-point was determined both colorimetrically and potentiometrically. How the potentiometric end-points were determined from the titration curves is described under Discussion.

It is mentioned below that the stainless steel electrode was found suitable for rapid direct titrations to the equivalence-point potential[25]. The procedure for such a titration was similar to that already described except that the buret was not weighed until the equivalence point was reached, as shown by a large deflection of the galvanometer. Colorimetric end-points could not be taken in these rapid potentiometric titrations.

RESULTS AND DISCUSSION

The potential of the stainless steel indicator electrode becomes constant quickly after each addition of the permanganate solution until near the end-point when 3–4 min are necessary for the attainment of a steady value. Similar time-dependence is known with the platinum electrode[2,26,27].

A typical plot of the potential (*E*) *vs.* total weight of the permanganate solution added (*W*) is given in Fig. 1. The end-point is taken where the maximum $\Delta E/\Delta W$[28] occurs. A summary of the results of all titrations is given in Table I. These show that the results by the colorimetric weight-titration method (*A*) and the potentiometric weight-titration procedure (*B*) agree well, since the average value of the ratio *A*/*B*

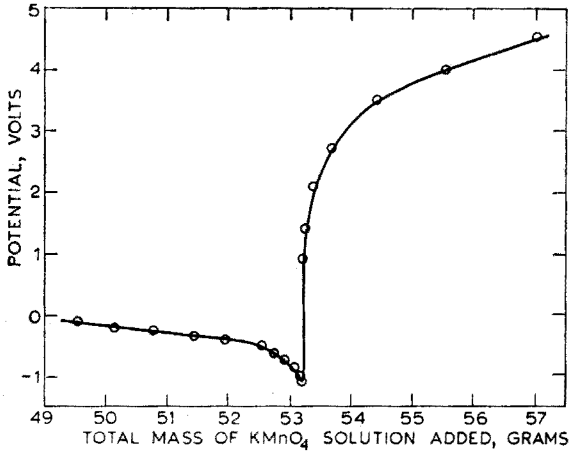

Fig. 1. Potentiometric weight-titration of hydrogen peroxide with 0.3224% (w/w) potassium permanganate; typical plot of potential in V *vs.* total mass of potassium permanganate solution added in g.

TABLE I

HYDROGEN PEROXIDE CONCENTRATION DETERMINATIONS

	H_2O_2 Concentration[a] *% (w/w)*			*Deviations*		
Stock solution no.	*Colorimetric method with no electrode*	*Potentiometric* *From potentiometric end-point*	*Colorimetric* *From colorimetric end-point*	*Deviation of B from average of (A + B) %*	*Deviation of C from average of (A + C) %*	*Deviation of B from average of (B + C) %*
	A[e]	*B*[e]	*C*[e]	*E*[f]	*F*[f]	*G*[f]
1	98.657 ±0.033	98.565 ±0.027	98.593 ±0.032	0.047	0.032	0.014
2[c]	95.194[b] ±0.006	95.145 ±0.030	95.194 ±0.029	0.026	0.000	0.025
3	98.472 ±0.032	98.616 ±0.069	98.649 ±0.068	0.073	0.089	0.016
4	98.731 ±0.033	98.725[b] ±0.024	98.755 ±0.010	0.003	0.012	0.015
5[d]	99.914[b] ±0.060	99.959 ±0.053	99.961 ±0.054	0.022	0.023	0.001
6	98.571 ±0.048	98.568 ±0.046	98.584 ±0.042	0.002	0.006	0.008
7	98.714[b] ±0.023	98.737 ±0.051	98.738 ±0.044	0.011	0.012	0.001

[a] Average of three titrations. The ± terms in this Table and elsewhere represent absolute standard deviations.
[b] Average of two titrations.
[c] Originally 98% (w/w) H_2O_2, more than two years old.
[d] Twice recrystallized 98% (w/w) H_2O_2.
[e] The average of the values of the ratios *A/B*, *B/C* and *A/C* are, respectively, 0.99991±0.00070, 0.99977±0.00018, and 0.99968±0.00075.
[f] The average of colums E, F and G are, respectively, 0.026%, 0.025% and 0.011%. The average % deviation from the average of all the runs of HUCKABA AND KEYES is 0.052% omitting their Run 6, and 0.159% including Run 6.

for all the stock solutions is 0.99991±0.00070. This is similar to the results of the comparison by HUCKABA AND KEYES[13] of the colorimetric weight-titration method with the absolute gasometric method*. The results by the colorimetric (*C*) and potentiometric (*B*) weight-titrations are in good agreement also, the average value of *B/C* being 0.99977±0.00018. The fact that the standard deviation for *B/C* is less than that for the average *A/B* value is not unexpected because *B* and *C* were determined at the same time. The average value of the ratio *A/C*, 0.99968±0.00075, supports the conclusion that the electrode causes no detectable decomposition of the hydrogen peroxide.

Rapid, direct titrations to the equivalence-point potential[18,25]

The occurrence of the very sharp potential jump at the end-point following a slow decrease makes it possible to titrate directly to the equivalence-point potential[25], so

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* The average value of the ratio of concentration determined by the gasometric procedure to that found colorimetrically was 0.99964±0.00173 (rejecting Run 6) or 0.99755±0.00682 (with Run 6)[13].

reducing the time necessary for precise work since only two weighings of the buret are necessary. Table II summarises the results of typical rapid titrations and amply demonstrates the success of the method.

TABLE II

COMPARISON OF THE RAPID POTENTIOMETRIC PROCEDURE WITH THE STANDARD COLORIMETRIC METHOD

Stock solution no.	*H_2O_2 Concentration*[a] % *(w/w)* *Colorimetric method with no electrode* *A*[b]	*H_2O_2 Concentration*[a] % *(w/w)* *Potentiometric method* *B*[b]	*Deviation of B from average of (A + B)* %
1	98.637 ±0.060	98.579 ±0.035	0.029
2	98.632 ±0.001	98.774 ±0.005	0.072
3	98.660 ±0.026	98.650 ±0.046	0.005

[a] Average of two titrations.

[b] The average of the values of the ratio *A/B* is 0.99975±0.00106.

Characteristics of the potentiometric titration

Fig. 1 shows that *E* at first falls slightly as *W* increases, the rate of change, $\Delta E/\Delta W$, becoming increasingly negative. Near the colorimetric end-point, *E* increases sharply; $\Delta E/\Delta W$ changes sign abruptly and attains a maximum value, $(\Delta E/\Delta W)_{\max}$, immediately, indicating the true end-point[28]. This behavior is similar to that found for the potentiometric titration (platinum, N-calomel) of aqueous hydrogen peroxide with ceric sulphate in the presence of hydrochloric acid[2]. Beyond the end-point the dependence of *E* on *W* is similar to the usual potentiometric curves[14].

Nature of the potential change and the factors affecting it

The magnitude of $(\Delta E/\Delta W)_{\max}$ depends somewhat on the electrode surface. With a fresh piece of steel electrode polished both mechanically and electrolytically, $(\Delta E/\Delta W)_{\max}$ was 6.2±1.6 V per g of 0.02 *M* potassium permanganate solution (average of 6 results). After standing unused for four months the electrode gave irreproducible results. On further electropolishing the reproducibility was restored but $(\Delta E/\Delta W)_{\max}$ was found to be only 3.0±1.2 V per g of 0.02 *M* potassium permanganate solution (average of 14 results). For a second stainless steel electrode prepared in the same way, except that the electropolishing was omitted, the $(\Delta E/\Delta W)_{\max}$ was 2.5±1.1 V per g of 0.02 *M* potassium permanganate solution (average of 2 results). After electropolishing and conditioning once again, the $(\Delta E/\Delta W)_{\max}$ was found to be 5.6±0.2 V per g of 0.02 *M* potassium permanganate solution (average of 3 results). This newly polished electrode and the older repolished electrode were compared by using them both separately to measure simultaneously the potential change for the same solution. In the region of excess hydrogen peroxide, the potentials registered by the two electrodes agreed fairly closely, within 2–3%, while a significant difference appeared only at and beyond the end-point, *i.e.*, in the region of excess permanganate. It appears that electropolishing is not only important for rendering the electrode passive[17] towards hydrogen peroxide solution but also for greater potential sensitivity of the electrode.

The $(\Delta E/\Delta W)_{max}$ values registered by the stainless steel electrode are comparable to those registered by platinum (*e.g.* 3–6 V per g of 0.1 *M* ceric sulphate solution[2]) or by gold (*e.g.* 3–4 V per g of 0.18 *M* sodium nitrite solution or *ca.* 8.0 V per g of 0.036 *M* potassium permanganate solution[7]).

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SUMMARY

The preparation and use of a stainless steel indicator electrode in the accurate potentiometric titration of aqueous hydrogen peroxide are described. The results agree excellently with those obtained by a standard colorimetric weight-titration procedure. The nature of the titration curves, potential changes and the factors affecting them are discussed. Rapid potentiometric titrations directly to the equivalence-point potential are possible, owing to the nature of the titration curve.

RÉSUMÉ

Une description est donnée sur la préparation et l'utilisation d'une électrode indicatrice en acier inoxydable, pour le titrage potentiométrique précis du peroxyde d'hydrogène. La nature des courbes de titrage, des changements de potentiels et l'influence de divers facteurs sont examinés. Des titrages potentiométriques rapides, directement au potentiel du point d'équivalence sont possibles, suivant la nature de la courbe de titrage.

ZUSAMMENFASSUNG

Es wird die Herstellung und Anwendung einer Indikator-Elektrode aus rostfreiem Stahl für genaue potentiometrische Titrationen von wässrigen Wasserstoffperoxydlösungen beschrieben. Die erhaltenen Ergebnisse stimmen gut überein mit denen, die nach der Standardmethode (colorimetrische Gewichtstitration) erhalten wurden. Der Verlauf der Titrationskurven, Potentialänderungen und die diese beeinflussenden Faktoren werden diskutiert. Rasche potentiometrische Titrationen bis direkt zum Aequivalenzpunkts-Potential sind möglich.

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DETERMINATION OF ORGANIC PERACIDS AND HYDROGEN PEROXIDE IN MIXTURES

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Organic peracids are of increasing importance in industry and research. Usually these acids occur in mixtures with hydrogen peroxide because of the manufacturing process or because of contact with aqueous systems; this raises the analytical problem of determining these substances in presence of each other. The present paper describes a simple analytical procedure for this purpose.

HATCHER AND HOLDEN[1] and other investigators[2-4] have previously shown that organic peracids and hydrogen peroxide can be determined in their mixtures. The determination was based on the facts that only peracids react rapidly and completely with neutral aqueous potassium iodide and that hydrogen peroxide is readily oxidised by potassium permanganate or ceric sulphate. Organic peracids usually do not interfere with permanganate titrations of hydrogen peroxide, but the latter may cause errors in iodometric determinations of peracids. To minimise such errors, low temperature, low acidity and rapid titration proved essential. Even with these precautions, the end-point tended to be slow and difficult to see.

The starting point for the present investigation was the idea that the above-mentioned difficulties might be overcome by the addition of a reagent which rendered hydrogen peroxide less reactive towards iodide during the titration of peracid. Such an additive is titanyl sulphate which forms a complex with hydrogen peroxide.

It was found that the presence of the titanyl reagent strongly retarded the reaction between the iodide and hydrogen peroxide without interfering with the determination of peracid. Thus a sharp end-point in the peracid titration could be obtained, without acidity, temperature or titration rate being of critical importance.

It would be very useful to be able to determine both peroxidic substances in the same sample by one analytical method, *i.e.* iodometrically, and consequently to employ sodium thiosulphate as the only standard reagent. To achieve this the hydrogen peroxide must be made available for reaction with iodide again after the titration of peracid. Here well-known facts were exploited: fluoride ions rapidly decolourise peroxytitanyl solutions and molybdic acid accelerates the reaction between hydrogen peroxide and iodide ions. It follows that our method consists of two subsequent titrations with thiosulphate.

For mixtures of performic acid and hydrogen peroxide the new method is of special value since the hydrolysis of performic acid:

$$H.COOOH + H_2O \rightarrow H.COOH + H_2O_2$$

is fairly rapid at room temperature. The direct determination of hydrogen peroxide by permanganate or ceric sulphate titration is associated with large errors partly because of hydrolysis and partly owing to the oxidation of formic acid by these titrants. In the present method, however, the sample is pipetted (or weighed) into an aqueous solution of potassium iodide and titanyl sulphate so that the peracid reacts instantaneously with iodide, and the hydrogen peroxide with titanyl ions. The two peroxidic compounds are thus "separated" before hydrolysis can occur.

If the mixture to be analysed is concentrated (highly active), a suitable solvent may be required for dilution. The solvent must be inert towards peroxidic compounds, incapable of forming peroxides itself with molecular oxygen, and miscible with water. *tert.*-Butyl alcohol seems to fulfil these requirements, but has the drawback of being solid at room temperature (m.p. 25.5°). Mixed with minor amounts of trimethylacetic acid, which is another suitable solvent for our purposes, it liquefies and can be used in the analytical procedure. Such solutions of peracids and hydrogen peroxide have shown a good degree of stability.

PRELIMINARY INVESTIGATIONS

In Table I are recorded iodometric titrations of three peracids with and without addition of titanium reagent. The peracids were actually mixtures with the corresponding carboxylic acids and 5.00 ml samples of these solutions were employed. Only in the case of performic acid was there a small difference in titration volumes caused by the presence of hydrogen peroxide in this acid.

TABLE I

TITRATION OF PERACIDS ONLY

Peracid	*ml thiosulphate used*	
	Ordinary titration	*+ 10 ml titanium reagent*
Performic	5.7	5.6
Peracetic	10.6	10.6
Perpropionic	5.2	5.2

In order to establish the optimum conditions for an analytical procedure, the effects of different additives on the titration values were studied by systematic variation of one factor at a time. In all experiments the same amount of hydrogen peroxide solution was employed, the correct titration value of which was 11.2 ml of 0.01 *N* sodium thiosulphate. There was no need to titrate mixtures of hydrogen peroxide and peracid in these cases since the only additive present during peracid titration, titanium reagent, was, as mentioned, without effect on the results.

Titanium reagent solution. The optimum amount was found to be 10 ml. On either side of this value the amount of titrant required decreased. With less than 10 ml this was due to the low acidity of the titrated solution, since the sole source of acid was the titanium reagent. (Checks were made with a solution containing the same concentration of sulphuric acid as the titanium reagent, and 10 ml was found to be the minimum value.) With more than 10 ml, the ratio of titanium to fluoride becomes too large to secure a complete liberation of hydrogen peroxide.

Sodium fluoride. The optimum amount was 0.3 g. On either side the amount of titrant required again decreased. With less than 0.3 g, the unfavorable titanium/fluoride ratio occurred again and above this value the reaction between iodide and peroxide was retarded.

Molybdic acid solution. The optimum amount was 25 ml, the amount of thiosulphate required decreasing on either side of this quantity.

Potassium iodide. The optimum amount was *ca.* 2 g. Rather wide variations in this amount were permissible.

Sodium tetrathionate. In the iodometric titration of peracids tetrathionate is formed, which owing to its reducing action interferes in the subsequent procedure, causing low results. The maximum permissible amount was found to be 10 ml of 0.01 *N* sodium tetrathionate.

Reaction time. The optimum reaction time was found to be 55 min. With times shorter than 50 min, the reaction was incomplete and with times longer than 60 min, the effect of even small amounts of tetrathionate became noticeable.

Reaction temperature. The optimum temperature proved to be 35°. Temperatures below 30° led to incomplete reaction, and temperatures above 40° led to low results.

Table II summarises some titrations of different peracids alone and in mixture with hydrogen peroxide. In the first horizontal row are given titration values for aliquots of samples 1–3 of hydrogen peroxide. The next row gives the titration values for aliquots of the samples 4–6 (performic, peracetic and perpropionic acid respectively). These peracids were, as is usually the case, in equilibrium with small amounts of

TABLE II

TITRATION OF HYDROGEN PEROXIDE AND PERACIDS, SEPARATELY AND IN MIXTURE

Hydrogen peroxide		*Sample 1*	*Sample 2*	*Sample 3*
ml thiosulphate used		9.4	9.0	11.9
Peracid		*Sample 4* *(performic)*	*Sample 5* *(peracetic)*	*Sample 6* *(perpropionic)*
ml thiosulphate used	Peracid	5.6	8.8	10.6
	H_2O_2[a]	0.1	0.8	0.8
Mixtures		*Sample 1 + 4*	*Sample 2 + 5*	*Sample 3 + 6*
ml thiosulphate used	Peracid	5.6	8.8	10.6
	H_2O_2	9.4	9.8	12.7

[a] Present as a contamination in the peracids.

TABLE III

FORMATION OF PERACIDS

Reaction mixture: Hydrogen peroxide (30%) 1.0 g, carboxylic acid 50 g, perchloric acid catalyst 0.1 ml. Temperature 20°. Titration of 1 ml samples.

Reaction time (min)	*ml thiosulphate required*		
	Formic acid	*Acetic acid*	*Propionic acid*
15	1.5	0.1	0.1
20	2.2	0.1	0.2
25	2.25	0.1	0.3
30	2.2	0.1	0.4
35	2.2	0.1	0.5
40	2.2	0.1	0.6
50	2.0	0.1	0.7
60	2.0	0.15	0.8
70	2.0	0.2	0.8
80	2.0	0.25	0.8
100	1.9	0.3	0.8
120	1.8	0.4	0.9
150	1.7	0.6	1.1
18h	1.7	1.5	1.6

hydrogen peroxide which were also determined. The last row shows the results obtained when mixtures of aliquots of different samples, *viz.* samples 1 + 4, 2 + 5 and 3 + 6, were analysed. The volume of titrant required for a peracid is the same as before, whereas for hydrogen peroxide it is the sum of the volumes required for the added peroxide and the peroxide present as a contamination in the peracid.

In Table III are given some results for the formation of peracids from hydrogen peroxide and the corresponding acids. In kinetic investigations of this kind the proposed method should prove of special value because the amounts of both reactants are "frozen" at the beginning of the analytical procedure. It can be seen that in the case of formic acid, the maximum amount of peracid was reached in 25 min. Acetic and propionic acids reacted much more slowly with hydrogen peroxide, equilibrium being reached only after 18 h.

RECOMMENDED METHOD

Reagents

Sodium thiosulphate, potassium iodide, sodium fluoride, hydrogen peroxide, formic, acetic and propionic acids were all of analytical grade.

Titanium reagent was prepared from recrystallised potassium titanyl oxalate by the method of Thornton and Roseman[5].

Iodide–starch solution: 10 g of potassium iodide and 1 g of starch per l.

Molybdic acid reagent: a saturated aqueous solution of molybdic acid anhydride.

Procedure

Weigh (pipet) a sample of the peroxidic mixture accurately and if necessary dissolve in *tert.*-butyl alcohol/trimethylacetic acid (20 : 1) in a volumetric flask. Add the sample or an aliquot to 300 ml of cold distilled water containing 25 ml of titanium reagent and 10 ml of iodide–starch solution. The presence of a peracid is indicated by an immediate blue coloration and the solution is titrated with 0.01 *N* thiosulphate. Hydrogen peroxide is indicated by a yellow to orange colour after the peracid titration is finished. At this point, add 0.30 g of sodium fluoride, 25 ml of molybdic acid solution and 2.0 g of potassium iodide. Store the solution at 35° for 55 min and again titrate with 0.01 *N* sodium thiosulphate.

The standard procedure was worked out for samples consuming a total of up to 25 ml of 0.01 N thiosulphate, ideally up to 10 ml for the peracid and up to 15 ml for hydrogen peroxide.

SUMMARY

A simple method for the determination of organic peracids and hydrogen peroxide in mixtures is presented. The method is based on the instantaneous reaction of peracids with neutral potassium iodide and on the formation of a stable complex between hydrogen peroxide and titanyl ions. This complex is decomposed with sodium fluoride and the ensuing reaction with iodide is accelerated with molybdic acid. The influence of the different additives on the analytical results has been studied.

RÉÉSUM

Une méthode simple est proposée pour le dosage de peracides organiques et de peroxyde d'hydrogène. Elle est basée sur la réaction des peracides avec l'iodure de potassium (titrage de l'iode formé par le thiosulfate) et la formation d'un complexe stable entre le peroxyde d'hydrogène et le titane (décomposition du complexe par addition de NaF, acide molybdique et iodure de potassium et titrage par le thiosulfate).

ZUSAMMENFASSUNG

Beschreibung einer einfachen Methode zur gleichzeitigen Bestimmung von Persäuren und Wasserstoffperoxyd. Sie beruht auf der Reaktion der Persäuren mit Kaliumjodid und der Bildung eines stabilen Komplexes zwischen Wasserstoffperoxyd und Titanylionen. Zunächst wird das durch die Persäuren ausgeschiedene Iod und anschliessend das durch Zugabe von Natriumfluorid, Kaliumjodid und Molybdänsäure gebildete Iod titriert.

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3,3′-DIHYDROXYBENZIDINE-N,N,N′,N′-TETRAACETIC ACID AS A METALLOFLUORESCENT INDICATOR IN EDTA TITRATIONS

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The use of the N,N,N′,N′-tetracarboxymethyl derivatives of several 3,3′-disubstituted benzidines as metallofluorescent indicators for compleximetric titrations has recently been recommended[1]. A general procedure was developed for the preparation of this type of compound in which the parent benzidines were condensed with sodium chloroacetate. The resulting tetraacetic acids were first isolated as their barium salts and then converted to tetrasodium salts which were further purified by fractional precipitation, or by conversion to the free acid and reprecipitation from ethanol using sodium ethoxide.

The preparation of 3,3′-dihydroxybenzidine-N,N,N′,N′-tetraacetic acid by this method was reported to be unsatisfactory, probably because of the very impure nature of the 3,3′-dihydroxybenzidine then available. As a result, this compound was not isolated or examined in any way. 3,3′-Dihydroxybenzidine can, however, be prepared from *o*-dianisidine by the method of BURKHARDT AND WOOD[2]. The pure, freshly prepared diamine readily undergoes condensation with sodium chloroacetate and the resulting tetraacetic acid can be isolated as its tetrasodium salt which can be purified by the procedure used by REES AND STEPHEN[1] for the purification of *o*-dianisidine-N,N,N′,N′-tetraacetic acid.

3,3′-Dihydroxybenzidine-N,N,N′,N′-tetraacetic acid in common with the other di-*ortho*-substituted benzidine tetraacetic acids in ultraviolet light shows an intense blue fluorescence at pH 4–10 which is quenched by certain metal ions. It was expected that the positioning of free hydroxyl groups adjacent to the imino-diacetic acid groups would improve the metallofluorescent properties by extending the range of metals which would quench the fluorescence. The applications of this compound as a metallofluorescent indicator were therefore examined.

EXPERIMENTAL

Preparation of 3,3′-dihydroxybenzidine[2]. *o*-Dianisidine (10 g) was dissolved in hydriodic acid (100 ml; d. 1.70) and the solution was refluxed at 138° for 24 h. The temperature was then raised and the unused hydriodic acid distilled off. The residue was dissolved in hot water and filtered, and sodium bisulphite solution was added to reduce the iodine present. Addition of aqueous sodium acetate to the solution gave a precipitate of the free base. This was filtered off, washed with boiling ethanol to remove unchanged *o*-dianisidine, and dried. The yield was 8 g of white amorphous material which rapidly darkened on exposure to air and light. The equivalent weight determined by non-aqueous titrimetry was 110 (calculated 108).

Preparation of 3,3'-dihydroxybenzidine-N,N,N',N'-tetraacetic acid (tetrasodium salt). 3,3'-Dihydroxybenzidine (6 g) was suspended in water (50 ml) and dissolved by the addition of sufficient dilute sodium hydroxide solution. Sodium chloroacetate (13 g) dissolved in water (60 ml) was added slowly with stirring over 1 h to the mixture warmed on a steam bath. Sodium hydroxide solution (2 *N*) was added as required to maintain the pH of the reaction mixture at about 8.0 (phenolphthalein). After about 2 h when no more sodium hydroxide solution was consumed, the mixture was filtered and a concentrated aqueous solution of barium chloride was added to the warm reaction mixture. The precipitated barium salt was digested on the water bath for some minutes, and then filtered off, washed with a small volume of water, and vacuum-dried. The barium content was determined by sulphate ashing (0.1277 g gave 0.0860 g of barium sulphate; calculated, 0.0831 g for a di-barium salt). The finely powdered barium salt was suspended in dry ethanol and the suspension was cooled in a mixture of salt and ice. A current of dry hydrogen chloride was then passed into the mixture until an excess was present. The precipitate of barium chloride was filtered off, and the filtrate was concentrated to half its bulk by distillation under reduced pressure. This concentrate was filtered into a fresh solution of sodium ethoxide in ethanol. The precipitate of the tetrasodium salt was filtered off, washed with a small quantity of ethanol and dried. Yield of grey powder 1.1 g. The sodium content determined from the sulphated ash was 24.1% (calculated 23.8%). The equivalent weight, determined by non-aqueous titrimetry, was 150 (calculated 145). The product was considered sufficiently pure for use in the analytical studies of its properties as an indicator.

The purity of the compound was confirmed by paper electrophoresis at pH 5 (acetate buffer). One major intense blue fluorescent spot and one very minor weakly fluorescent spot were observed when the electropherogram was examined by ultraviolet light.

Titration of copper or lead with EDTA

The source of ultraviolet light was described previously[3].

An intimate mixture of the tetrasodium salt of 3,3'-dihydroxybenzidine-N,N,N',N'-tetraacetic acid with potassium nitrate in the ratio 1 : 100 was used as the indicator.

Procedure. Ten ml of approximately 0.02 *M* metal ion solution was diluted to about 50 ml with water; 2–3 ml of aqueous 20% hexamine buffer solution (pH 6) and 5–10 mg of the solid indicator mixture were added. The titration was conducted in a darkened room with the solution exposed to the source of ultraviolet light. The solution was titrated with 0.02 *M* EDTA to the appearance of the blue fluorescence.

The copper solution was standardised using Fast Sulphon Black F as indicator[4]. The lead solution was standardised using Xylenol Orange as indicator[5].

Titration of manganese, zinc, cobalt and cadmium

Ten ml of approximately 0.02 *M* metal ion solution was diluted to approximately 50 ml with water, and sufficient hexamine buffer solution (pH 6.0) was added followed by 5–10 mg of indicator mixture and 2–3 drops of aqueous 0.01% Rhodamine B solution. The solution was titrated with 0.02 *M* EDTA until the fluorescence of the solution changed from pink to blue.

The reverse titrations were carried out following an identical procedure but with the metal ion as titrant.

RESULTS AND DISCUSSION

3,3′-Dihydroxybenzidine-N,N,N′,N′-tetraacetic acid exhibits a characteristic intense blue fluorescence in aqueous solutions exposed to ultraviolet light. Several cations, particularly copper(II) and lead(II), bring about a complete quenching of this fluorescence; many others cause only a partial quenching of the fluorescence. In view of this behaviour the new compound was examined as a metallofluorescent indicator for the compleximetric titration of metal ions with EDTA.

Titration of copper. Copper(II) solutions can be titrated satisfactorily with EDTA using the new indicator. A sharp end-point, denoted by the appearance of an intense blue fluorescence, is obtained between pH 4 and 10, although pH 6 is preferred. Sharp end-points, denoted by the disappearance of fluorescence, are also obtained in the reverse titration. Bi^{3+}, Cd^{2+}, Co^{2+}, Ce^{3+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Th^{4+}, Zr^{4+} and In^{3+} interfere with the titration by consuming the titrant. These ions do not affect the nature of the end-point, however, and can be titrated with an excess of EDTA, the excess being determined by titration with copper(II) in the presence of the indicator.

Titration of lead. Satisfactory end-points are obtained in the titration of lead with EDTA between pH 4 and 8 using the solid indicator mixture. The end-points in the reverse titration are also sharp. The following metal ions can be determined by titration of an excess of EDTA with lead: Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Bi^{3+}, Th^{4+}, In^{3+} and Zr^{4+}.

Titration of manganese, zinc, cobalt and cadmium. The addition of manganese, zinc, cobalt or cadmium to an aqueous solution of 3,3′-dihydroxybenzidine-N,N,N′,N′-tetraacetic acid does not completely quench its fluorescence. The end-point in the titration of these cations with EDTA is therefore not sharply defined, but it can be greatly improved by the addition of a suitably coloured fluorescent dyestuff to the solution to be titrated. This different fluorescence masks the weak fluorescence which remains when a slight excess of metal ion is present. A fluorescent dyestuff with a fluorescence colour of good contrast to that of the free indicator is used. The end-point in such titrations is then marked by a change in the colour of the fluorescence of the solution from that of the screening agent to that of the free indicator, or vice versa. This technique has been used in a previous study[6] to improve the end-point in the titration of the alkaline earth metals with EDTA using Calcein as indicator.

In the procedure adopted for the titration of manganese, zinc, cobalt and cadmium with EDTA at pH 6.0, Rhodamine B was found to be the most effective screening agent. The end-points in the titration of the metals were characterised by a change in the colour of the fluorescence of the solution from pale salmon-pink (*i.e.* the fluorescence of a very dilute solution of Rhodamine B) to pale blue.

Because the indicator itself binds metal ions, the indicator blank could be appreciable if an excessive amount of indicator were taken. The fluorescence of the indicator, however, is usually sufficiently intense to allow the use of very small quantities of the solid indicator mixture which eliminates the necessity to correct for an indicator blank. It is possible to detect the end-points in titrations of dilute solutions of metal ions more precisely than with many metallochromic indicators.

The results obtained with 3,3′-dihydroxybenzidine-N,N,N′,N′-tetraacetic acid as indicator in the direct and reverse titrations of copper(II) and lead(II) with EDTA were in excellent agreement with those obtained using the accepted metallochromic indicators. In fact, the titration of lead gave more consistent results (±0.01 ml of 0.02 M EDTA) with the metallofluorescent indicator than with the metallochromic indicator (Xylenol Orange).

3,3′-Dihydroxybenzidine-N,N,N′,N′-tetraacetic acid, unlike *o*-dianisidine-N,N,N′,-N′-tetraacetic acid[1], can be employed in the titration of metals other than copper(II). In particular, the titration of lead(II) has extended the usefulness of the metallofluorescent indicator systems. The free hydroxyl groups undoubtedly result in the formation of stronger metal–indicator complexes, as indicated by the increased number of metal ions which cause complete or nearly complete quenching. It is to be expected that further suitable substitution of the 5,5′-positions would result in even stronger metal–indicator complexes being formed and that specific indicator actions might then be obtained.

The intensity of the fluorescence of 3,3′-dihydroxybenzidine-N,N,N′,N′-tetraacetic acid is similar to that of the *o*-dianisidine analogue but the fluorescence is rather less vivid although not inferior with regard to the indicator action. The sensitivity of the indicator is much less than that of the 4,4′-diaminostilbene analogues recently described[3]. The latter compounds are more suitable as indicators for very dilute solutions but their action is limited to the titration of copper(II) with EDTA or the reverse titration.

SUMMARY

3,3′-Dihydroxybenzidine-N,N,N′,N′-tetraacetic acid has been prepared and examined as a metallofluorescent indicator in compleximetric titrations. Copper(II) and lead(II) are determined by titration with EDTA in the presence of the indicator, the blue fluorescence of which is restored at the end-point. Manganese, zinc, cobalt and cadmium can also be determined if a dyestuff such as Rhodamine B is present along with the indicator.

RÉSUMÉ

L'acide dihydroxy-3,3′-benzidine-N,N,N′,N′-tétracétique a été préparé et examiné en vue de son utilisation comme indicateur fluorescent. Il permet le dosage du cuivre et du plomb au moyen d'EDTA. Le manganèse, le zinc, le cobalt et le cadmium peuvent également être dosés de cette façon si l'on ajoute de la rhodamine B.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Eignung von 3,3′-Dihydroxybenzidin-N,N,N′,N′-tetraessigsäure als Fluoreszenzindikator bei der Titration von Kupfer und Blei mit EDTA. Bei Zusatz von Rhodamin B können auch Mangan, Zink, Kobalt und Cadmium bestimmt werden. Die Herstellung des Indikators wird beschrieben.

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ELIMINATION OF PHOSPHATE INTERFERENCE IN FLAME PHOTOMETRIC DETERMINATION OF STRONTIUM AND BARIUM

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The influence of phosphate and sulphate on the emission of calcium was reported in a previous study[1]; the maximum depression of the phosphate on the emission of calcium chloride occurred at an equimolar ratio of phosphate to calcium. Addition of lanthanum chloride or ferric chloride solution caused the intensity of the calcium line and bands (at 422.7, 554 and 622 mμ) to rise gradually back to the emission of pure calcium chloride. The effect of lanthanum was explained by the binding of phosphate with lanthanum, which leaves the calcium free.

In the present work the depressing influence of phosphate on the emissions of strontium, barium and lanthanum and the restoration of the strontium and barium emissions in the presence of lanthanum were studied. The chemical interactions of calcium, strontium or barium with phosphate and lanthanum, and the conditions of precipitation, evaporation and decomposition on heating were also examined. The latter results confirmed those obtained by flame spectrophotometry.

EXPERIMENTAL

Stock solutions

The following stock solutions were prepared:

(*1*) Strontium chloride: 2.0 mg Sr^{2+}/ml.
(*2*) Barium chloride: 10.0 mg Ba^{2+}/ml.
(*3*) Lanthanum chloride: 10.0 mg La^{3+}/ml.
(*4*) Phosphoric acid: 1.44 mg PO_4^{3-}/ml.

Flame photometry

A Beckman DU flame spectrophotometer was used to measure the emission of appropriate quantities of the stock solutions, previously acidified with hydrochloric acid to pH 0.5–1.5, in a 50-ml volumetric flask. A no. 156 Beckman red-sensitive phototube was used for the barium emission band at 873 mμ and a no. 4310 Beckman multiplier phototube for the strontium emission line at 460.7 mμ and for the lanthanum emission band at 560 mμ.

A 22 MΩ load resistor was used with the multiplier phototube and a 10.000 MΩ load resistor with the red-sensitive phototube.

Slit widths were 0.13 mm, 0.15 mm and 0.2 mm for strontium, barium and lanthanum respectively.

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Photomultiplier sensitivity was set to positions 2 and 3 for strontium and lanthanum respectively.

Both hydrogen and oxygen pressures were regulated to 8.0 lbs p.s.i.

A medium bore atomizer was used in all experiments.

Preliminary tests

Gradual addition of ammonia to an equimolar solution of lanthanum chloride and phosphoric acid until no phosphate was found in the filtrate, showed that phosphate was completely precipitated at pH 4.5. In further tests, ammonia was added to solutions containing calcium, strontium or barium plus phosphate and lanthanum in a molar ratio of 1 : 1 : 5 (Me : PO_4^{3-} : La), to give a pH of 4.5, and the precipitate was filtered and washed.

Analysis of the filtrates showed that all the calcium, strontium or barium was in the filtrate, while all the phosphate had been precipitated with lanthanum. When equimolar solutions of an alkaline earth metal with phosphate were evaporated on a hot plate, heated to 1000°C in a furnace for 1 h and then analyzed for metal ions and phosphate, it was found that the respective phosphates were converted to pyrophosphates. Decomposition of the pyrophosphates did not occur during further heating for 10 h at 1000°C.

When solutions containing equimolar amounts of phosphate and alkaline earth metal and of lanthanum (and phosphate) were dried in an oven at 140°C and then

TABLE I

WATER LEACHING AFTER HEATING AT 140°C

Ions introduced (mg)					*Molar ratio*		*Analyses of leach liquor*[a]				*Recovery of alkaline earth ions in leach liquor (%)*
Ca	*Sr*	*Ba*	*PO_4^{3-}*	*La*	*PO_4^{3-}/cation*	*La/PO_4^{3-}*	*Ca*	*Sr*	*Ba*	*La*	
197.0	—	—	496.0	695.0	1	1	180.0	—	—	30.0	90.0
—	448.0	—	496.0	695.0	1	1	—	416.5	—	14.0	92.0
—	—	685.0	496.0	695.0	1	1	—	—	667	not found	97.0
197.0	—	—	496.0	3200.0	1	5/1	200.0	—	—	—	101.5
—	448.0	—	496.0	3200.0	1	5/1	—	440.0	—	—	98.2
—	—	685.0	496.0	3200.0	1	5/1	—	—	654.0	2581	95.5

[a] Phosphate was not found.

TABLE II

MAXIMUM INTERFERENCE EFFECTS OF PHOSPHATE ON EMISSIONS OF VARIOUS CATIONS

Cation	*Emission (mμ)*	*Molar ratio PO_4^{3-}/cation*	*% residual emission of the cation*	*Molar ratio La^{3+}/PO_4^{3-} for maximum restoration of emission*
Ca^{2+}	554	1/1	38	3.5/1
Sr^{2+}	460.7	1/1	34	5/1
Ba^{2+}	873	1/1	34	4.5/1
La^{3+}	560	1/1	36	—

leached with distilled water, all the alkaline earth cation but no phosphate was found in the leach liquor (Table I). The same results were obtained using solutions containing equimolar amounts of phosphate and alkaline earth metal, the molar ratio of lanthanum to phosphate being 5.

RESULTS

Flame photometric work

Fig. 1 shows that the emission of standard samples of strontium, barium or lan-

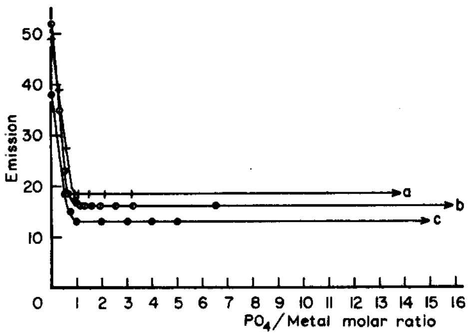

Fig. 1. Influence of phosphate on the emission of Sr, Ba and La. a = La; b = Sr; c = Ba.

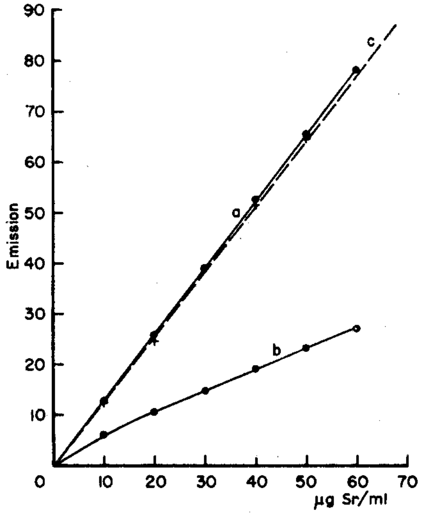

Fig. 2. Standard calibration curves for Sr. a = Sr; b = Sr + PO_4 (PO_4/Sr = 1/1); c = Sr + PO_4 + La (PO_4/Sr = 1/1; La/PO_4 = 5/1).

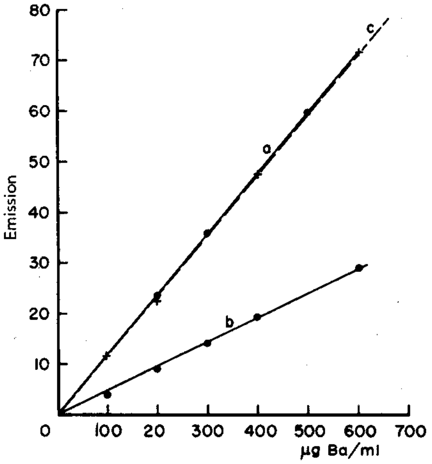

Fig. 3. Standard calibration curves for Ba. a = Ba; b = Ba + PO_4 (PO_4/Ba = 1/1); c = Ba + PO_4 + La (PO_4/Ba = 1/1; La/PO_4 = 5/1).

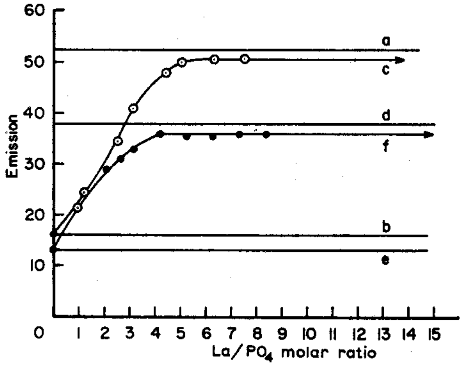

Fig. 4. Restoration of Sr and Ba emission in presence of phosphate by addition of lanthanum. a = $SrCl_2$; b = $SrCl_2$: H_3PO_4 (1/1); c = $SrCl_2$: H_3PO_4 (1/1) plus $LaCl_3$; d = $BaCl_2$; e = $BaCl_2$: H_3PO_4 (1/1); f = $BaCl_2$: H_3PO_4 (1/1) plus $LaCl_3$.

thanum decreased on addition of phosphate until equimolar amounts of phosphate and metal were reached. Further addition of phosphate did not affect the emission. With a fixed equimolar ratio of phosphate to metal, changing the concentrations of strontium and barium gave straight line plots for metal emission *vs.* metal concentration (Figs. 2 and 3). Thus the percentage of residual emission was constant at different concentrations of the same metal. Addition of lanthanum to solutions containing equimolar ratios of strontium or barium phosphate caused the metal emissions to increase to the initial emission values of the metal chloride solutions (see Fig. 4). In both cases, a molar ratio of lanthanum to phosphate of 4–5 was necessary to restore the emission completely. The experimental results and those obtained previously for calcium[1] are summarized in Table II.

DISCUSSION

The chemical experiments indicate that acid solutions of calcium, strontium or barium phosphate, when atomized through the warm direct sprayer, vaporize along the length of the atomizer with the formation of a stable pyrophosphate which enters the flame. The pyrophosphates of the alkaline earth metals are partially decomposed only at the higher temperatures of the flame (about 2500°K) and the residual emission of calcium, strontium or barium comes only from the thermal decomposition of the pyrophosphate.

The restoring effect of lanthanum on the emission of calcium, strontium or barium in the presence of phosphate shows that the same reactions govern all three cations. The chemical experiments show that lanthanum phosphate, being less soluble, is formed before the alkaline earth phosphate, so that in the presence of lanthanum, the calcium, strontium or barium reaches the flame free from phosphate. Lanthanum must be added in a molar ratio of lanthanum to phosphate of approximately 5 to ensure a maximum recovery of the cation.

These results agree well with those obtained by ALKEMADE AND VOORHUIS[2] who used two direct sprayers connected in parallel; when calcium chloride solution was sprayed into the flame through one, while phosphoric acid was sprayed through the other, no depression of calcium emission was found. This means that calcium phosphate is not formed in the flame, but before arriving in the flame.

It can be concluded that the effects which are important in the formation and suppression of anionic interference in flame photometry are primarily of a chemical nature. The chemical effects, which are governed by the equilibrium constant of the reaction, the solubility product and the acidity of the solutions, appear in the sprayed solution before its arrival into the hot region of the flame. In the decrease of the cationic emission by formation of phosphate, the principal effect is the thermal decomposition in the flame of the alkaline earth phosphate. In the restoration of the emission by addition of lanthanum, the principal effect is the formation of stable lanthanum phosphate before the flame is reached; this allows the alkaline earth metal to reach the flame free of phosphate.

SUMMARY

The interference of phosphate in the flame emission of calcium, strontium and barium was studied. The emission intensity decreases proportionally to the amount of interfering anion up to a maximum depression for equimolar amounts of phosphate to metal. A thermostable phosphate is

formed before the cation enters the flame. Appropriate addition of lanthanum restores the three alkaline earth lines to their intensities in absence of phosphate, the lanthanum displacing the alkaline earths from their phosphates before the hot region of the flame is reached.

RÉSUMÉ

L'influence du phosphate lors du dosage du calcium, du strontium et du baryum, par photométrie de flamme, a été examinée. La diminution d'intensité de l'émission est proportionnelle à la teneur de l'anion gênant. Le lanthane déplace les alcalino-terreux de leurs phosphates et ainsi permet de retrouver l'intensité (obtenue en l'absence de phosphate) de ces trois éléments.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den störenden Einfluss von Phosphat bei der flammenphotometrischen Bestimmung von Calcium, Strontium und Barium. Es wurde gefunden, dass die durch Phosphat verursachte Abnahme der Emissionsintensität durch Zugabe von Lanthan verhindert werden kann.

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THE USE OF THE METHOD OF CONTINUOUS VARIATION FOR THE CLASSIFICATION OF COMPLEXES WITH MOLE RATIO 1:1

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The method of continuous variation, originally described by Ostromisslensky[1] and Job[2], is frequently employed for determining the mole ratio between reactants forming a complex. A critical study of the applicability of the method of continuous variation was published recently by Asmus[3,4].

The present paper deals with the use of the method of continuous variation for classifying complexes of the form A_mB_n where $m/n = 1$. It is demonstrated theoretically and experimentally that from curves of continuous variation, it is possible to distinguish between two groups of complexes with mole ratio 1:1; one group comprises complexes for which $m = n = 1$, and another group contains those for which $m = n > 1$.

THEORY

Considering the equilibrium

$$mA + nB \rightleftharpoons A_mB_n \qquad (1)$$

Ostromisslensky and Job showed that a curve expressing the concentration of the complex, or a quantity proportional to the concentration, as a function of the mole fraction x, exhibited a maximum for

$$x = n/(m + n)$$

In his investigations of the applicability of the method of continuous variation, ASMUS only studied equilibria in which $m = 1$. He demonstrated that for reactions in which $m = 1$ and $n > 1$, the curves of continuous variation exhibited inflections for small values of x. For values of x below those corresponding to the inflections, the curves were parabolas with zero gradient at $x = 0$. Curves in the vicinity of $x = 1$ did not exhibit inflections and at $x = 1$ the gradients assumed finite values. For complexes in which $m = n = 1$, ASMUS showed that the curves of continuous variation had no inflections and that the gradients at $x = 0$ and $x = 1$ were different from zero.

It was considered to be of interest to extend ASMUS' investigations by studying equilibria in which $m > 1$.

The law of mass action may be applied to equation (1):

$$k = \frac{[A_mB_n]}{[A]^m[B]^n} \tag{2}$$

If c represents the constant total concentration of reactants ($c = c_A + c_B$), and x the mole fraction ($x = c_B/(c_A + c_B)$) then the equilibrium concentrations of A and B are

$$[A] = c(1 - x) - m[A_mB_n] \tag{3}$$

$$[B] = cx - n[A_mB_n] \tag{4}$$

From equations 2, 3 and 4,

$$\frac{1}{k}\cdot[A_mB_n] = (c(1 - x) - m[A_mB_n])^m\,(cx - n[A_mB_n])^n \tag{5}$$

Introducing $[A_mB_n]/c = y$, equation (5) can be written

$$f(x,y) = (1-x-my)^m\,(x - ny)^n - \frac{1}{kc^{m+n-1}}\,y = 0 \tag{6}$$

For $m = 1$, this equation corresponds to the expression developed and discussed by ASMUS. By differentiating equation (6)

$$\frac{dy}{dx} = -\frac{\frac{\partial f}{\partial x}}{\frac{\partial f}{\partial y}} = \frac{(1 - x - my)^{m-1}(x - ny)^{n-1}(n - (m + n)x)}{(1 - x - my)^{m-1}(x - ny)^{n-1}(n^2 + (m^2 - n^2)x - mn(m + n)y) + 1/(kc^{m+n-1})} \tag{7}$$

For this expression $dy/dx = 0$ for $x = n/(m + n)$ corresponding to the maximum in the curves of continuous variation.

For $m = n = 1$ and $x = 0$ or $x = 1$, equation (7) becomes

$$\frac{dy}{dx} = \frac{1}{1 + 1/kc}$$

This expression has been reported previously by SCHWARZENBACH[5].

For $m = n > 1$, however, $dy/dx = 0$ also for $x = 0$ or $x = 1$. Thus, when a curve of continuous variation is plotted and a maximum at the mole fraction $x = 0.5$ is obtained, then the presence or absence of inflections and the form and gradients of the curve for values of x near zero and one may give information about the group of 1 : 1 complex present.

A curve which exhibits inflections and is parabolic for values of x near zero and one, and which has zero gradient at $x = 0$ and $x = 1$, indicates the presence of a complex with $m = n > 1$. On the other hand, the absence of inflections and parabolic portions, as well as the presence of a finite gradient at $x = 0$ and $x = 1$, indicates a complex with $m = n = 1$.

It should be noted, however, that for complexes of high stability belonging to the group $m = n > 1$, the inflections and parabolic portions of the curve may not be visible. In the vicinity of $x = 0$ and $x = 1$, experimental errors may also make the detection difficult. For complexes of low and intermediate stability it should, however, be possible to distinguish between the two groups.

In Fig. 1 theoretical curves of continuous variation are plotted for two complexes of composition A_2B_2 and stability constants $k_1 = 2.5 \cdot 10^{15}$ and $k_2 = 1.65 \cdot 10^{16}$. Equation (6) was used in the calculations, a graphical method being used to solve the equations of fourth degree. Both complexes in Fig. 1 exhibit the expected inflections and parabolic form for values of x near zero and one. In the figure tangents to the curves are also drawn.

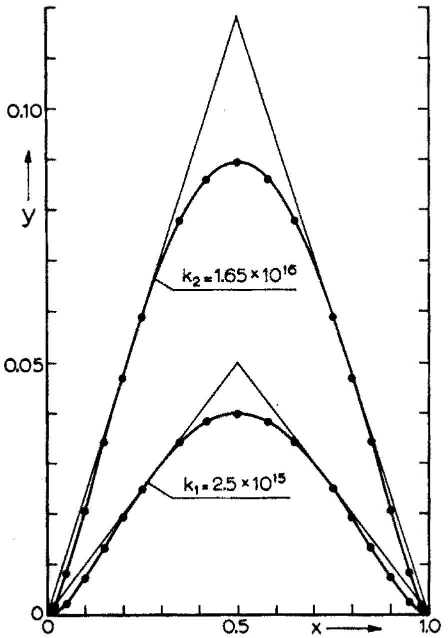

Fig. 1. Theoretical curves of continuous variation for two complexes of composition A_2B_2 with stability constants $k_1 = 2.5 \cdot 10^{15}$ and $k_2 = 1.65 \cdot 10^{16}$. The sum of concentrations of reactants ($c = c_A + c_B$) was $0.8 \cdot 10^{-5}$ M.

EXPERIMENTAL

The method described above was tested on the system iron(III)–chrome azurol S. This system was investigated by the authors (the results will be published later) and was found to contain four complexes (apart from hydroxo complexes).

In solutions of pH about 3.5 containing metal and ligand in equimolar amounts, and in mixtures with a small excess of one of the reactants, a ring-formed complex consisting of two metal atoms and two ligand molecules was found to predominate. This complex is designated the intermediate complex. From potentiometric measurements, the absolute stability constant of the intermediate complex was calculated to be $6 \cdot 10^{35}$. On the basis of this value, the conditional constant at pH 3.40 was calculated to be $2 \cdot 10^{16}$.

On changing the pH to below 3.0, a complex containing one iron(III) atom and one ligand molecule seemed to be formed.

In the presence of comparatively large excesses of either metal ion or ligand, complexes composed of two metal atoms and one ligand molecule, and of one metal atom and two ligand molecules were detected, respectively.

The method of continuous variation was employed to determine the mole ratio of the intermediate complex, and a distinct maximum at the mole fraction 0.5 was attained, corresponding to a mole ratio of 1 : 1. A detailed curve of continuous variation was then plotted for values of x near zero and one. The experimental details were as follows. Into two series of 100-ml volumetric flasks, 10 ml of 1.0 M potassium chloride solution, a volume v_1 of 10^{-3} M iron(III) solution and a volume v_2 of 10^{-3} M chrome azurol S solution were transferred. For all mixtures $v_1 + v_2 = 0.80$ ml. After dilution to a volume of about 99 ml, the pH was adjusted to 3.40 by addition of sodium

TABLE I

EXPERIMENTAL DATA FOR A CURVE OF CONTINUOUS VARIATION

Concentrations (molarity $\cdot 10^5$) of		*Mole fraction*	*Total extinction observed*	*Correction due to the ligand*	*Difference*
iron(III)	*chrome azurol S*				
0.024	0.776	0.030	0.293	0.283	0.010
0.040	0.760	0.050	0.291	0.277	0.014
0.048	0.752	0.060	0.298	0.274	0.024
0.056	0.744	0.070	0.303	0.272	0.031
0.064	0.736	0.080	0.302	0.269	0.033
0.072	0.728	0.090	0.299	0.266	0.033
0.080	0.720	0.100	0.296	0.263	0.033
0.096	0.704	0.120	0.302	0.258	0.044
0.110	0.690	0.137	0.311	0.252	0.059
0.160	0.640	0.200	0.328	0.234	0.094
0.200	0.600	0.250	0.346	0.220	0.126
0.600	0.200	0.750	0.193	0.073	0.120
0.640	0.160	0.800	0.152	0.058	0.094
0.705	0.095	0.881	0.091	0.034	0.057
0.720	0.080	0.900	0.075	0.028	0.047
0.730	0.070	0.912	0.069	0.025	0.044
0.737	0.063	0.921	0.063	0.022	0.041

hydroxide solution. The solutions were finally diluted to volume with distilled water. Mixtures were prepared in the mole fraction ranges $0.03 < x < 0.25$ and $0.75 < x < 0.92$.

The extinctions were measured against a blank of distilled water using 5.000-cm cells at a wavelength of 570 mμ, which is near the absorption maximum of the intermediate complex. The extinction data were corrected in the normal way by subtracting the extinctions due to the amount of ligand added originally. This contribution was calculated after a determination of the molar extinction coefficient for chrome azurol S at pH 3.40 and in the presence of 0.10 M potassium chloride.

The experimental data are given in Table I, and the resulting curve in Fig. 2. The experimental curve of Fig. 2 may be compared with the theoretical curves shown in Fig. 1. The curve in Fig. 2 exhibits two inflections. All points on the left-hand branch are below the tangent indicating the parabolic approach to $x = 0$. On the right-hand branch the points on the upper part of the curve are also below the tangent. The points on the lower part did not, however, indicate the group $m = n > 1$. In these mixtures comparatively large amounts of a complex of one ligand molecule and two iron atoms probably obscured the expected effects. In this range it may also be more difficult to attain equilibrium conditions. On the whole, the curve indicated the presence of a complex of the group $m = n > 1$.

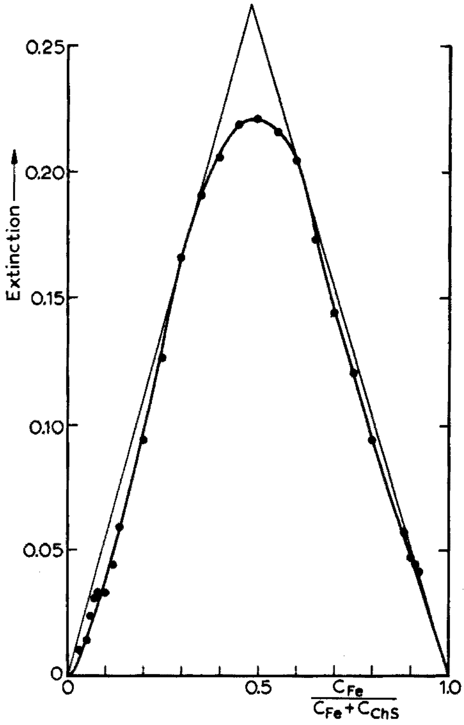

Fig. 2. Experimental curve of continuous variation for the system iron(III)–chrome azurol S. The pH of the solutions was 3.40. Wavelength 570 mμ. $c = c_{Fe} + c_{ChS} = 0.80 \cdot 10^{-5}$ M. 5.000-cm cells.

SUMMARY

It is shown theoretically and experimentally that curves of continuous variation may be used to classify complexes of the form A_mB_n for which $m/n = 1$, into two different groups: one group comprises complexes for which $m = n = 1$, and another group contains those for which $m = n > 1$.

The system iron(III)–chrome azurol S was used to demonstrate the applicability of the method.

RÉSUMÉ

Il est démontré théoriquement et expérimentalement que des courbes de variation continue peuvent être utilisées pour classer des complexes de la forme A_mB_n, pour lesquels $m/n = 1$, en deux groupes: (*1*) un groupe comprenant des complexes pour lesquels $m = n = 1$ et (*2*) un groupe renfermant ceux pour qui $m = n > 1$.

Le système fer(III)–chrome azurol S est choisi pour démontrer l'applicabilité de la méthode.

ZUSAMMENFASSUNG

Es wird theoretisch und experimentell gezeigt, das Kurven von kontinuierlichen Variationen nach Job zur Einteilung von Komplexen der Form A_mB_n (bei $m/n = 1$) in zwei Gruppen angewandt werden können: Eine Gruppe von Komplexen für welche $m = n = 1$ und eine zweite Gruppe, für die $m = n > 1$ ist.

Zum Nachweis der Anwendbarkeit dieser Methode wurde das System Eisen-(III)–Chromazurol S verwendet.

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THE USE OF IMPREGNATED FILTERS TO COLLECT TRACES OF GASES IN THE ATMOSPHERE

PART II. COLLECTION OF SULFUR DIOXIDE ON MEMBRANE FILTERS

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In a preceding paper[1], the significance and utility of using impregnated filters as collecting devices for gases were examined. The nature of membrane filters and the theoretical and practical suitability of Millipore* filters as a substrate was evaluated.

Sulfur dioxide was selected as the initial gas to be used for development and evaluation of the methodology. The continuing interest in sulfur dioxide as an atmospheric constituent and the availability of sensitive and selective analytical methods for its determination dictated its selection. In this paper the methodology and effects of impregnating filters are examined. The apparatus and procedures used in preparation and sampling known concentrations of sulfur dioxide in air are detailed. The results obtained when known concentrations are sampled using impregnated filters are evaluated. It is planned that future papers in this series will detail the analytical methodology and results obtained from atmospheric sampling.

EXPERIMENTAL

Filter impregnation

After preliminary experiments with assorted filter types, impregnating solutions

TABLE I

COMPARISON OF ABSORPTION BY SELECTED FILTERS AND PHYSICAL PARAMETERS

	A	*B*	*C*	*D*	*E*	*B/D·E*
Filter type	*Wt. salt absorbed (mg)*	*Wt. sol. absorbed (mg)*	*Mean wt. filter (mg)*	*Filter thickness* (μ)	*Porosity (%)*	
	1% Sodium bicarbonate solution					
AA	1.2	231	78	150	82	1.9
HA	0.8	216	108	150	79	1.8
VM	0.2	142	86	130	72	1.5
	5% Sodium bicarbonate solution					
AA	7.9	236	80	150	82	1.9
HA	7.1	224	108	150	79	1.9
VM	4.5	144	85	130	72	1.5

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* Trademarked designation of membrane filters marketed by Millipore Corp., Bedford, Mass.

and procedures, the filter and solution combinations shown in Table I were selected for intensive evaluation.

Procedures

Filter impregnation. The detailed procedure used to impregnate filters was as follows.

Fill a shallow container such as a Petri dish to a depth of 0.5 inch with the impregnating solution. With forceps, take the filter face up and touch the back of the filter to the solution. Release the filter, which should float on the surface of the solution. The solution should not touch the face of the filter. As soon as the filter is filled with solution, shown by the filter becoming uniformly translucent, lift the filter from the solution and place face up on an absorbent pad. Place an additional absorbent pad on the face of the filter and press gently. Remove the top pad and place the filter face up in a desiccator.

The above procedure was appropriately modified when filter weights, weights of solution absorbed, or weight of impregnant were desired.

Solution take-up. The amount of solution taken up by the filters is given in Table I. The amount of solid phase on the filter, as shown, was determined by the weight increase after drying. In order to check the results obtained, the apparent solution concentration was calculated from the weights of the absorbed solution and solid impregnant.

With filters impregnated with bicarbonate, constant weight was reached within

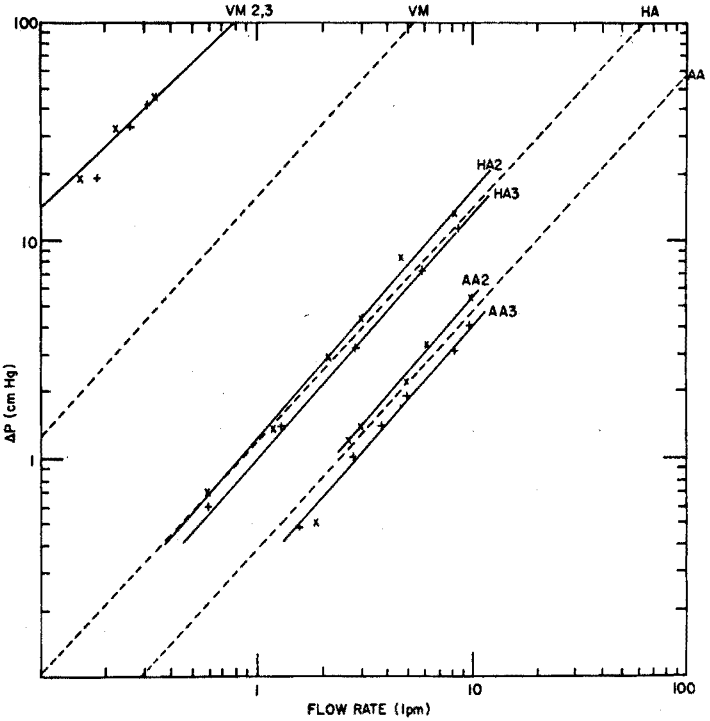

Fig. 1. Pressure drop and flow rate for impregnated filters.

48 h after drying over "Drierite", as evidenced by no further change in weight of the filters during the subsequent week.

The available pore volume in the filter was contrasted with properties of the various types of filters as shown in Table I. Of the combinations examined, only B/D·E, as shown, shows a consistent pattern. The amount of solution absorbed can thus be postulated to be a function of pore volume, with a quantitative and consistent difference in the nature of AA, HA, and VM filters. This symmetry is not found when A/D·E is examined, indicating that the difference in solute and solvent take-up by the filters is an actual phenomenon. It is postulated that solvation of the filter material might account for this preferential absorption.

Effect of impregnation on flow rate. The flow rate and associated pressure drops were determined for the sodium bicarbonate-impregnated filters. The resulting data are shown graphically in Fig. 1, together with dashed curves for the equivalent non-impregnated filters. It is seen that impregnation does not greatly affect the HA and AA filters, but plugs the VM filter so as seriously to limit the usefulness of this type for air sampling. This agrees with the conclusion of GOETZ[2] that 200 $\mu g/cm^2$ of cadmium sulfide can be deposited within a membrane filter without changing its permeability appreciably.

Preparation and sampling of known concentrations

The apparatus used is shown schematically in Fig. 2. All tubing used in the apparatus was glass or Teflon. Although the apparatus was constructed as a closed system as shown, the preparation and sampling steps were conducted at separate times by means of manipulation of appropriate valves.

Preparation of known concentrations. The portion of the apparatus used for prepar-

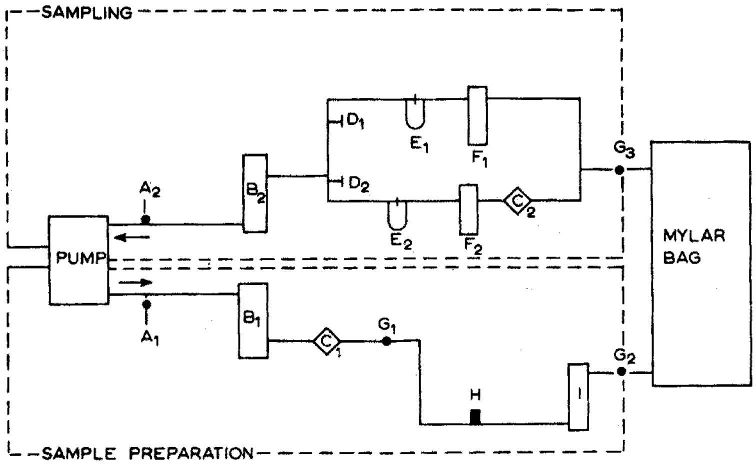

Fig. 2. Schematic of apparatus for preparation and sampling known concentrations.

ing known concentrations is enclosed in a dashed line designated "sample preparation" in Fig. 2. The drying tube (B1) contained calcium sulfate or silica gel in all sulfur dioxide runs, since the carbon dioxide content of the air was to be maintained. The filter holder (C1) contained an AA Millipore filter. The flowmeter (I) contained glass and sapphire balls only, to eliminate any possibility of reaction with the gases being used. The Mylar bag had a volume of approximately 120 l.

The flowmeter was calibrated under conditions of use (atmospheric pressure approximately 630 mm Hg), by inserting a wet test meter between stopcock (G2) and the Mylar bag. As an example of the procedure used, 100 l of a 1 p.p.m. concentration of SO_2 (one part of sulfur dioxide per million parts of air by volume) was prepared as follows.

The bag was filled using a flow of 10 l per min; when the bag was half full, 0.1 ml of sulfur dioxide contained in a gas-tight hypodermic syringe, was injected through septum (H). When 10 min had elapsed, the bag was closed and kneaded. The bag was emptied and refilled several times. Once the bag had been pre-conditioned and was in frequent use, only one filling was required. For operation after a period of disuse, a full pre-conditioning cycle should be followed[3]. This should consist of at least six refills, with at least one overnight period when the bag is filled with the nominal concentration desired.

The volume and flow rates used were selected on a basis of convenience. Since both the flow rate given by the flowmeter and the volume of gas in the hypodermic syringe were determined at ambient temperature and pressure, simple volume ratios without correction could be used to prepare concentrations in p.p.m.

Sampling known concentrations. The portion of the apparatus enclosed in the broken line designated "sampling" in Fig. 2 was used for sampling known concentrations. For sulfur dioxide runs, trap (B2) contained Ascarite as an absorbent. D1 and D2 are Hoke series 280 valves with vernier handwheels. E1 and E2 are orifice flowmeters which are calibrated at 1 l per min or other appropriate flow rate. These meters are calibrated for each set of collectors used unless the change in resistance has been shown to have a negligible effect on the flow rates. F1 and F2 are collectors which in most cases will be bubblers. F1 is used as a reference collector for assaying the gas stream.

F2 and C2 comprise a test collection unit for the type of run used in most of the experimental work. Various combinations of collectors may be substituted as dictated by the specific requirements of various experiments.

Known concentrations of sulfur dioxide in air previously prepared in the Mylar bag were sampled by matching flows through the parallel sampling lines by means of valves D1 and D2 and flowmeters E1 and E2. Sodium tetrachloromercurate(II) was used as the collection solution and the samples were analyzed by the WEST AND GAEKE method[4].

RESULTS

Evaluation of the sampling apparatus

The experimental design and effect of introducing collector components into the system were evaluated by introducing various combinations into the system. The results obtained are shown in Table II. It is seen that when sampling sulfur dioxide, introduction of a filter holder or a Millipore filter before the collector does not decrease the amount of sulfur dioxide collected.

In order to minimize the quantity of sampling solution required, Ace Glass Co. #I-1050 bubblers were used as the reference collectors. All other collectors were compared to these bubblers. As shown in Table II, two runs were made in which two bubblers in series were used in the test collection lag of the apparatus. Within experimental error (estimated at ± 3%) the bubblers with tetrachloromercurate solution were found to be 100% efficient in removing sulfur dioxide.

TABLE II

MICROGRAMS OF SO_2 IN TEST AND REFERENCE COLLECTORS WHEN USING VARIOUS COMBINATIONS OF COLLECTOR COMPONENTS

Collectors are designated as C, F_1 and F_2 as shown in Fig. 2. Sample volume for series A, B and C was 10 l; for series D, E and F, 30 l.

Test collector description	*Series*	*Reference (F_1) collector*	*Test (F_2) collector*
Without filter holder (C)	A	0.68	0.68
With (C) – no filter	A	0.73	0.68
With (C) – plain AA filter	B	0.41	0.50
With (C) – TCM filter	A	0.73	0.68
	B	0.50	0.41
	D	0.51	0.45
With (C) – HCO_3^- filter	B	0.41	0
	E	0.36	0.009
	F	0.63	0.024
Two bubblers in series	B	—	0.41–0
	C	—	0.34–0

Comparison of actual and nominal prepared concentrations

The method used to prepare known concentrations of sulfur dioxide in Mylar bags is subject to the usual errors inherent in static systems. Of these, the most important are errors in flow rates when filling bags, syringe manipulations and reaction of the gas with components of the system. Therefore, the concentrations actually obtained, as shown by assays, were examined. The results obtained are given in Table III.

Except for the freshly prepared 0.1 p.p.m. concentration, the actual concentrations obtained were found to be low by 20%. This was not consistent, however, as shown by the relatively large (15–30%) standard deviation of different preparations of the same nominal concentration. The data validate our early assumption that each bag preparation should be assayed and that the nominal concentration should not be relied on.

Despite the above, the 10 p.p.m. means of assayed values show a surprising, although perhaps fortuitous, coincidence. This would tend to discount aging and loss effects when a 10 p.p.m. concentration is stored and thus corroborate the conclusions reached by ALTSHULLER *et al.*[3].

Where more than one assay was carried out for a single preparation, the percentage standard deviation was computed for each group of assays, and the mean calculated for each nominal concentration. As shown in Table III, the precision for a group of assays can be good, but generally tends to be erratic. This probably reflects errors in sampling time. Where the system is used to determine collection efficiency independent of the actual concentrations, the lack of precision is not very important.

TABLE III

COMPARISON OF ACTUAL *VS.* NOMINAL CONCENTRATIONS OF SULFUR DIOXIDE PREPARED IN MYLAR BAGS

Numbers in parentheses are number of assays performed to yield the mean value given.

Nominal concentration (p.p.m.)	*Sulfur dioxide found by assay*							
	Freshly prepared		*Aged 24 h*		*Aged 48 h*		*Aged 72 h*	
	p.p.m.	*% Std. dev.*	*p.p.m.*	*% Std. dev.*	*p.p.m.*	*% Std. dev.*	*p.p.m.*	*% Std. dev.*
0.1	0.098 (3)	4						
	0.126 (2)	1	0.087 (3)	9				
	0.097							
		3*						
	0.107	15**						
1.0	0.80 (3)	1						
	0.94 (3)	10						
	0.86 (3)	10						
	0.70 (3)	19						
	1.18 (2)	8						
	0.71 (2)	9						
	0.38 (2)	26	0.98 (3)	2				
	0.44 (2)	13						
	1.06 (2)	20						
	0.95							
	1.02	13*						
	0.48							
	1.06							
	0.81	32**						
10	8.3 (2)	1	6.2 (3)	2				
	8.8 (2)	3	7.9 (3)	11	7.8 (3)	6	7.7 (3)	10
	9.4		8.3 (3)	20				
	8.0							
	7.9	2*		11*				
	8.7							
	6.8		7.5	15**				
	7.2							
	9.6							
	5.6							
	5.5							
	8.1							
	7.8	17**						

* Mean % standard deviation of multiple analyses of single preparations.
** Mean % standard deviation of assays.

Collection efficiency of filters

Filters impregnated with potassium bicarbonate or sodium tetrachloromercurate(II) (TCM) were used in a series of tests to determine collection efficiency, using the techniques described above. As indicated, the collection efficiency was calculated by

$$CE = 1 - \frac{\text{concn. found in bubbler after filters}}{\text{concn. found in bubbler parallel with filter}}$$

The results in Table IV indicate that a TCM filter is ineffective in removing sulfur dioxide (collection efficiency less than 10%) but that a bicarbonate-impregnated

TABLE IV

COLLECTION EFFICIENCY OF IMPREGNATED FILTERS FOR SULFUR DIOXIDE

Values shown are means of the number of determinations given in parentheses following the value.

Impregnant	*Liters sampled*	*Filter*	*Collection efficiency (%)*			
			Sulfur dioxide concentration (p.p.m.)			
			0.1	*0.5*	*1.0*	*10*
TCM	15	AA	—	5	7	—
$KHCO_3$	15	AA	97 (7)	96 (3)	97 (7)	>96 (12)
		HA	—	—	99	—
	30	AA	97	96	99	94 (2)
	60	AA	98	89	98	90 (2)

filter is better than 95% efficient. The lower collection efficiencies for some bicarbonate filters were presumed to be a function of the collector capacity, as shown below.

Capacity of impregnated filters

The cumulative collection of sulfur dioxide on a filter with time is shown in Fig. 3 for 0.1, 1 and 10 p.p.m., up to capacity. Capacities are calculated on the basis that an impregnated HA filter contains 11 mg of potassium bicarbonate (AA = 12 mg), equivalent to 7,150 µg (3,250 l at 1 p.p.m.) of sulfur dioxide.

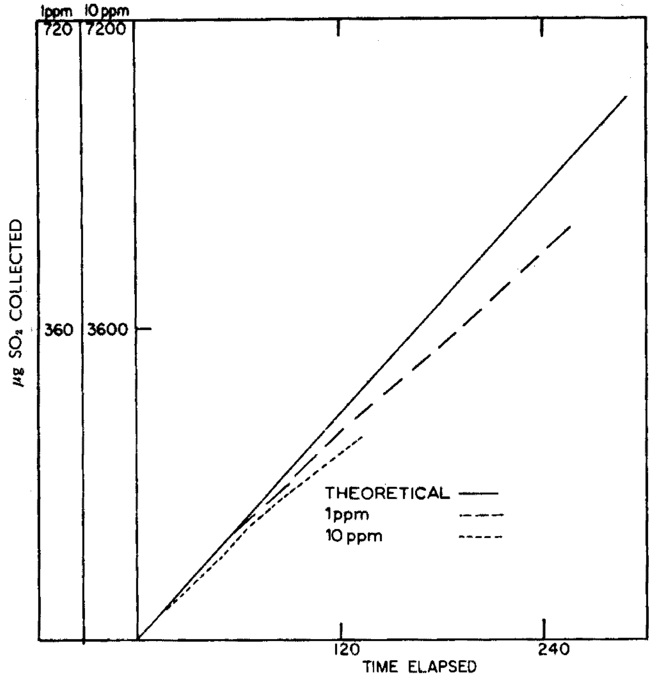

Fig. 3. Theoretical *vs.* actual capacity of impregnated filters for sulfur dioxide.

The actual capacities of impregnated filters were determined by sampling successive preparations through the same filter and determining the amount collected after each preparation, in the usual manner. The results shown in Table IV indicate that the theoretical capacity is not approached before a loss of collection efficiency becomes significant. Nonetheless, the usable capacity is sufficient to sample a 10 p.p.m. concentration for over an hour without an appreciable decrease in collection efficiency. Lower concentrations may be sampled for appropriately longer times.

Some of the experimental data indicated that the impregnated filters have a regenerative capacity when sampling is carried out intermittently. This datum and the limited capacity of the impregnated filters tend to confirm the assumption that collection takes place on the surface of the impregnant.

The assistance of Helen A. Huitt, National Center for Atmospheric Research, in many phases of the experimental work is gratefully acknowledged.

SUMMARY

HA and AA Millipore filters impregnated with 5% potassium bicarbonate and dried were found to be suitable for sampling concentrations of sulfur dioxide in air. The impregnation technique and filter loadings are described; flow rates are relatively unaffected by impregnation. The apparatus and procedures used for preparation and sampling known concentrations of sulfur dioxide in air are described. Comparisons of actual and theoretical concentrations in the 0.1 to 10 p.p.m. range showed that the concentrations prepared must be assayed.

The collection efficiency of impregnated filters was evaluated for sodium tetrachloromercurate-(II) (less than 10% which is in contrast with the 100% efficiency found with TCM as a scrubbing solution) and potassium bicarbonate (greater than 95%). The capacity of the filters was such that sampling a 10 p.p.m. sample for at least 1 h is possible.

RÉSUMÉ

L'emploi de filtres imprégnés de bicarbonate de potassium convient pour le prélèvement de traces d'anhydride sulfureux dans l'atmosphère. La méthode d'imprégnation et la charge des filtres sont décrites, de même que l'appareillage et les procédés utilisés pour la préparation d'échantillons de concentrations connues de SO_2 dans l'air. L'efficacité des filtres imprégnés a été évaluée à $> 95\%$ pour le bicarbonate de potassium; tandis qu'elle est $< 10\%$ pour le tétrachloromercurate(II).

ZUSAMMENFASSUNG

Es wird gezeigt, dass Filterpapier, welches mit Kaliumbicarbonat imprägniert ist, zur Bestimmung des Schwefeldioxydgehaltes der Luft sehr gut geeignet ist. Bei Versuchen mit Luft von bekanntem Schwefeldioxydgehalt wurde festgestellt, dass mehr als 95% absorbiert wurden. Die Herstellung der imprägnierten Filter, deren Anwendung sowie die notwendige Apparatur werden beschrieben.

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THE SAMPLING OF SULFUR DIOXIDE IN AIR WITH IMPREGNATED FILTER PAPER

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The most widely used devices for the sampling of gaseous atmospheric pollutants are impingers and bubblers. These absorbers have some disadvantages which are most felt in field work, such as fragility and the difficulty of handling the liquid content. It was therefore considered desirable to use solid absorbers. STRATMANN[1] developed an interesting method for the determination of sulfur dioxide in which the gas is adsorbed on silica gel; it is later desorbed in the laboratory at a high temperature and reduced to hydrogen sulfide, which can be determined by very sensitive methods. The STRATMANN method is, however, rather elaborate and there seems to be no constant supply of the special silica gel which is difficult to prepare.

In this paper a method is presented for the collection of sulfur dioxide using filter paper impregnated with solutions; most of the advantages of liquid and solid absorbents are combined. Previous workers[2,3] have utilized the coloration or bleaching of impregnated filter paper by sulfur dioxide for its determination. In our method, however, the sulfur dioxide is collected very efficiently on the paper and can be washed out in the laboratory and determined by any convenient method. Thus a higher precision and sensitivity can be attained.

The possibility of collecting gaseous air pollutants on filter paper was suggested by the observation that normal wet filter paper supported on sintered glass is capable of retaining a relatively large part of the sulfur dioxide present in the air that is drawn through it. This interfered with the determination of sulfuric acid mist in the atmosphere, for which the arrangement was intended.

In preliminary tests, we tried filter paper prepared with a large percentage of silica gel, such as that used by OKKERSE[4] for the determination of certain organic vapours. In experiments with these filters highly efficient collection was obtained with filters which also contained sodium hydroxide. Surprisingly, common filter paper treated in the same way was not only as efficient but the sulfur dioxide once absorbed proved to be quite resistant to atmospheric oxidation.

Further improvements gave an impregnated filter paper with very useful properties, such as high efficiency of collection under almost all circumstances and good stability of the collected sulfur dioxide.

An application that suggested itself was the semi-continuous sampling of sulfur dioxide with a filter-tape air-sampler; this was found to be possible and is the more important because there is a tendency to express MAC-values for air pollutants as the mean over, *e.g.*, 30 min.

It appears that an analogous use can be made of impregnated filter paper for the collection of air pollutants other than sulfur dioxide; successful applications to the sampling of hydrogen fluoride and hydrogen sulfide will be reported at a later date.

EXPERIMENTAL

The impregnated filter may be considered as an absorber in which a small amount of liquid is finely divided on a solid support, hence the air that is drawn through the absorber will have a much greater effect than in the case of impingers. For this reason, the influence of the humidity and the carbon dioxide of the air on the collection efficiency of the filters and on the stability of the retained sulfur dioxide was investigated.

A second important point is the oxidation velocity of retained sulfur dioxide. Several impregnating liquids were investigated in these two respects and the best were studied more fully.

Impregnating liquids. Solutions of the following substances in water were tested.

(*1*) Potassium hydroxide, potassium carbonate and potassium bicarbonate: carbonate and bicarbonate were included because the hydroxide changes slowly to these salts in contact with air; the potassium salts were chosen because they are more hygroscopic than the corresponding sodium salts.

(*2*) The same salts with the addition of glycerol: glycerol is said to have a stabilizing effect on sulfur dioxide[5]; also it is hygroscopic.

(*3*) The same salts with the addition of potassium chloromercurate: the latter is known to stabilize sulfite[6]. In the case of hydroxide extra potassium iodide, and in the case of carbonate extra potassium chloride, was required to keep the mercury complex in solution. Of course this had an adverse effect on the stability of the sulfite complex.

(*4*) The same salts as in (*3*) with the addition of glycerol.

(*5*) The same salts as in (*1*) with the addition of triethanolamine, which was found to be preferable to glycerol in some respects.

(*6*) Calcium chloride in order to see whether alkali was indispensable.

(*7*) Calcium chloride with sodium chloromercurate.

Filters. Whatman No. 1; diam. 5.5 cm. These were prepared by bathing them in the impregnating solutions, excess of which was squeezed out with a common household wringer. After this procedure the filters contained about 13 mg of solution/cm^2. Finally they were dried in an oven, usually at 110°.

Bicarbonate filters were prepared by keeping carbonate filters for a few days in a carbon dioxide-rich atmosphere.

Sampling procedure. The air containing sulfur dioxide was drawn through the filters usually at a rate of 1 m^3/h. The filters were clamped between plastic rings in a holder. The rings restricted the effective diameter of the filters to 4 cm and sometimes two or three filters were used in series in the same holder. The air flows were measured by rotameters and/or dry test meters.

Air streams with known or approximately known quantities of sulfur dioxide were prepared in two ways:

(*a*) by means of a dosing stopcock and mixing chamber. This gave an unknown but rather high concentration during a short time. The total quantity of sulfur dioxide was a few hundred micrograms. The device was used in the determination of collection efficiencies.

(*b*) by mixing a small stream of sulfur dioxide measured by a rotameter with a large stream (1,000 m^3/h) of air, measured by means of a plate-orifice meter.

Control of the relative humidity of the air. This was achieved in two ways:

(*a*) by diminishing the pressure. The humidity was then calculated from the residual pressure and the humidity and pressure of the laboratory air. This procedure is not quite correct because the collection efficiency may depend on the pressure via the diffusion velocity. However, diffusion in the gas phase does not seem to be a limiting factor. Nevertheless, this procedure was used only in the preliminary investigations.

(*b*) by mixing measured streams of laboratory air and air completely dried by means of silica gel. This procedure was checked by means of a wet and dry bulb hygrometer and was found to be sound.

Determination of the sulfur dioxide absorbed. The sulfur dioxide was determined by the *p*-rosaniline method[7] in the washings of the filters after addition of an amount of acid just sufficient to neutralize the alkaline content of the filters.

Collection efficiency. The efficiency η of the filters was determined in two ways:

(*a*) from the quantities of sulfur dioxide, F_1 and F_2 respectively, found on the first and second of two filters in series, by means of the formula

$$\eta = 1 - F_2/F_1$$

This is only approximately correct because there is a slight difference in the humidity and velocity of the air at the two filters, caused by the pressure drop over the first filter. Therefore this procedure was used only in the preliminary investigations.

(*b*) from the quantities of sulfur dioxide, F and I, found respectively on a filter and an impinger in series, by the formula:

$$\eta = \frac{F}{F + 1.04\,I}$$

The factor 1.04 was calculated from the collection efficiency of the impinger, which was found to be 96%, independent of the humidity.

Determination of stability. The stability of the absorbed sulfur dioxide was determined by storing filters with known quantities of sulfur dioxide in a desiccator over dry silica gel or over water saturated with sodium chloride to maintain a humidity of 75%. The quantities of sulfur dioxide contained in the filters were calculated from the volume of air drawn through them, the sulfur dioxide concentration of the air being determined in a parallel test.

RESULTS

It was found that at high humidities all filters had sampling efficiencies of at least 99% except those that were impregnated with a solution containing 25% calcium chloride in water or in 30% sodium chloromercurate solution. These absorbed less than 10% of the quantity of sulfur dioxide drawn through them. The efficiency of the others dropped markedly below 100% at relative humidities below 30%. In Table I are shown the efficiencies found at 25% humidity; the figures are the mean of two

TABLE I

SAMPLING EFFICIENCIES OF IMPREGNATED FILTER PAPER AT 25% RELATIVE HUMIDITY

Impregnating solution		*Efficiency*
Solutions in water	20% KOH	80
	10% K_2CO_3	48
	17·5% K_2CO_3	68
	25% K_2CO_3	59
	37·5% K_2CO_3	52
	50% K_2CO_3	54
	25% $KHCO_3$	5
	8% KOH + 10% $HgCl_2$ + 40% KI	41
	8% K_2CO_3 + 10% $HgCl_2$ + 30% KCl	10
Solutions also containing 10% glycerol	20% KOH	96
	25% K_2CO_3	95
	35% $KHCO_3$	93
	15% K_2CO_3 + 2% $HgCl_2$ + 12% KCl	89
20% KOH + 10% triethanolamine in water		98

TABLE II

PERCENTAGE OF SULFUR DIOXIDE LEFT AFTER STORING THE FILTERS AT 75% HUMIDITY

Impregnating solution	*Time of storage (days)*					
	1	*3*	*4*	*7*	*14*	*28*
KOH	93	—	—	0	—	—
K_2CO_3	42	10	—	0	—	—
KOH + glycerol	96	—	—	0	—	—
K_2CO_3 + glycerol	70	—	17	0	—	—
K_2CO_3 + $HgCl_2$ + KCl + glycerol	—	65	50	35	20	9
KOH + $HgCl_2$ + KI + glycerol	7	—	3	—	—	—
KOH + triethanolamine	see Fig. 1					

TABLE III

PERCENTAGE OF SULFUR DIOXIDE LEFT AFTER STORING THE FILTERS OVER SILICA GEL

Impregnating solution	*Time of storage (days)*					
	1	*7*	*9*	*21*	*28*	*51*
KOH	105	100	—	—	104	—
K_2CO_3	98	101	—	—	103	—
KOH + glycerol	96	107	—	—	105	—
K_2CO_3 + glycerol	99	106	—	—	103	—
K_2CO_3 + $HgCl_2$ + KCl + glycerol	—	97	—	103	—	—
KOH + triethanolamine	—	—	98	106	—	96

determinations. It can be seen from Table 1 that filters impregnated with solutions containing glycerol or triethanolamine gave the most satisfactory results. Apparently, the efficiency did not depend very much on the total quantity of potassium carbonate. Filters with a high quantity of alkali were stiff when dry and very wet at high humidity, but had a high sampling capacity. Impregnating solutions containing 20% potassium hydroxide or 25% potassium carbonate gave a reasonable compromise.

In Tables II and III are given the results of experiments on the rate of atmospheric oxidation of the sampled sulfur dioxide. These figures are incomplete but show that there was no advantage in the use of impregnating solutions containing mercury compounds. The other filters were equally suitable when kept dry. In a humid atmosphere, the potassium hydroxide filters were markedly better, but even these could not be kept for longer than one day if the sulfur dioxide was to be determined as such. Of course it could always be determined as sulfate. To summarize: of the impregnating solutions investigated, those containing 20% potassium hydroxide and 10% glycerol or triethanolamine were the most suitable; they had the best collection efficiencies at low humidity and the best stabilizing effect on the retained sulfur dioxide. They were therefore studied further.

Figure 1 shows that the rate of oxidation of sulfur dioxide absorbed on filters was low at first but increased later. It was considered that the effect might have been connected with the uptake of carbon dioxide, but the results of an experiment conducted in a carbon dioxide-free atmosphere suggested no such connection and this line of investigation was not further followed.

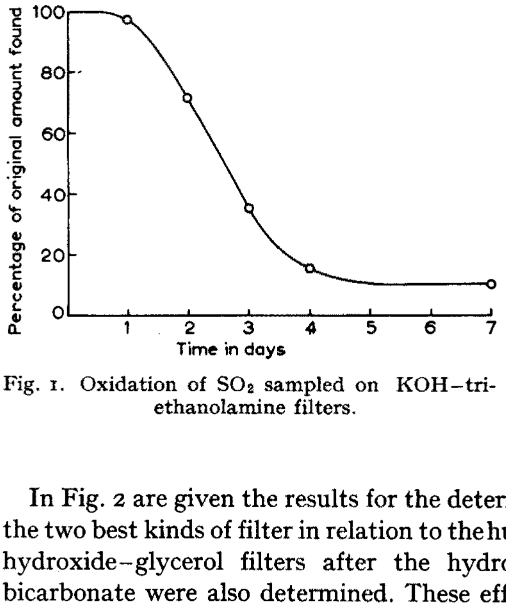

Fig. 1. Oxidation of SO_2 sampled on KOH–triethanolamine filters.

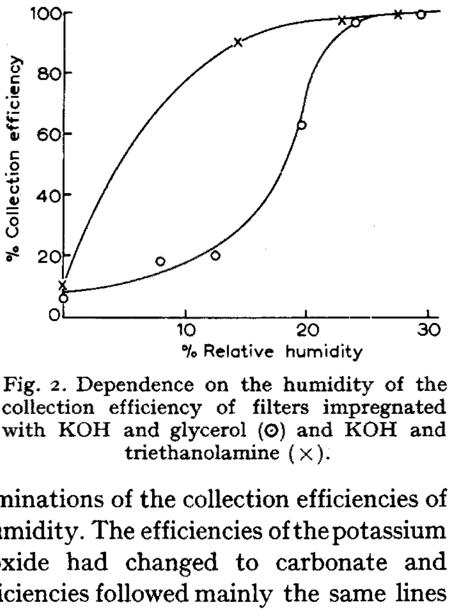

Fig. 2. Dependence on the humidity of the collection efficiency of filters impregnated with KOH and glycerol (○) and KOH and triethanolamine (×).

In Fig. 2 are given the results for the determinations of the collection efficiencies of the two best kinds of filter in relation to the humidity. The efficiencies of the potassium hydroxide–glycerol filters after the hydroxide had changed to carbonate and bicarbonate were also determined. These efficiencies followed mainly the same lines as those of the original filters, but, parallel with an increase in the percentage of carbon dioxide, efficiencies became to an increasing extent dependent on the total quantity of sulfur dioxide. The potassium bicarbonate–glycerol filters, for instance, showed an efficiency of 91% at a humidity of 17% with a total collected quantity of 300 μg of sulfur dioxide, but an efficiency of only 79% at a humidity of 37% with 2.5 mg of sulfur dioxide collected.

The hydroxide on the filters changed to bicarbonate only very slowly. Table IV summarizes some of the results. No doubt the rate of carbon dioxide uptake would vary with the humidity. These results were obtained at a humidity of about 50%.

Another effect of the restriction in the amount of absorbing solution was a limited sampling capacity, *i.e.* the sampling efficiency was dependent on the total collected

TABLE IV

COMPOSITION OF THE ALKALI OF THE FILTERS IN % EQUIVALENT AFTER DRAWING AIR THROUGH

Impregnating solution	*Time of treatment with air (days)*	*% OH^-*	*% CO_3^{2-}*	*% HCO_3^-*
KOH+	0	93	7	0
glycerol	1	0	91	9
	10	0	78	22
KOH +	0	86	14	0
triethanol-	1	0	89	11
amine	10	0	50	50

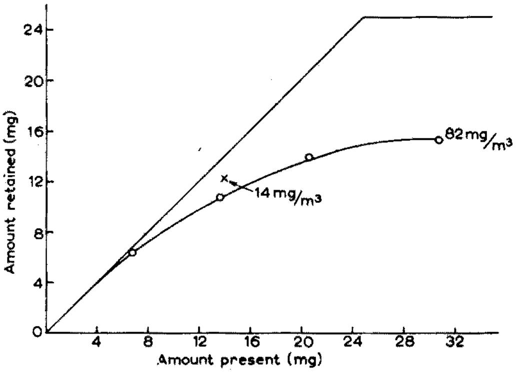

Fig. 3. Quantity of SO_2 collected compared with the quantity present in the air drawn through the filters.

quantity of sulfur dioxide. Figure 3 shows this dependence at a humidity of 45%; the straight lines represent the ideal 100% efficiency until all the hydroxide is consumed according to the reaction

$$2\ KOH + SO_2 \rightarrow K_2SO_3 + H_2O$$

It can be seen from Fig. 3 that the efficiency depends not only on the total quantity of sulfur dioxide, but also on its concentration.

The above-mentioned experiments cover sufficient ground to give an idea of the possibilities and limitations of the impregnated filter paper method.

Applications. To investigate the technique more fully, we devised what we term a "limits test". In these tests the filters were subjected to a combination of the most adverse circumstances under which the method can still be used. These limiting conditions were chosen rather arbitrarily in such way that in practice it should normally be possible to remain on the safe side. The conditions were as follows:

(*a*) Concentration of sulfur dioxide: 10 mg/m³,

(*b*) Total quantity of sulfur dioxide: 10% of the theoretical filter capacity according to (*1*),

(*c*) Relative humidity: 30% and 25% for the potassium hydroxide–glycerol and the potassium hydroxide–triethanolamine filters, respectively,

(*d*) Air velocity: 50 l/cm²/h.

This "limits test" was used to study four possible applications of the impregnated filter paper method, *viz.* to replace impingers or bubblers in: (*1*) short-time measurements, lasting, *e.g.*, 30 min; (*2*) medium-time measurements, lasting, *e.g.*, one day; (*3*) long-time measurements lasting, *e.g.*, ten days; (*4*) sequential samplers.

In the testing of application (*1*) the test was carried out immediately after preparation of the filters; after the test the filters were kept in a desiccator for 3 days before analysis (representing a week-end).

Application (*2*) was tested in two ways: (*a*) The test was applied immediately after the preparation of the filters as in (*1*) but then laboratory air was drawn through the filters for 1 day before they were kept dry for 3 days; (*b*) air was drawn through for one day, then the test was applied and then the filters were kept dry for 3 days.

Tests of application (*3*) were done as for (*2b*) except that air was drawn through the filters for 10 days.

In order to calculate the collection efficiency, three filters in series were used, the last one being a freshly prepared potassium hydroxide–triethanolamine filter. In order to calculate the loss of sulfur dioxide during the three days the concentration was determined in parallel with freshly prepared potassium hydroxide–triethanolamine filters. All tests were done in duplicate.

To illustrate application (*4*), an A.I.S.I. automatic smoke sampler was modified in such way that the filter tape was always in a closed compartment dried with silica gel. The tape itself was impregnated with potassium hydroxide–triethanolamine solution before use. The sampler was set to take 30-min samples of outdoor air during 10 days. Each working day the limits test was applied to two successive spots by feeding air containing about 10 mg SO_2/m^3 during two successive 15-min periods. However, the humidity was always higher, sometimes much higher than 30%. The filter tape was analysed after another 10 days in a desiccator.

TABLE V

RESULTS OF THE "LIMITS TEST"

Impregnating solution	*Days air drawn through*		*% SO_2 on*		*% found after 3 days*
	Before test	*After test*	*First filter*	*First plus second filter*	
KOH + glycerol	0	0	92	99.8	91
	1	0	53	89	99
	0	1	92	99.8	101.5
	10	0	37	65	75
KOH + triethanolamine	0	0	92	99.7	99
	1	0	81	97	97
	0	1	90	99.9	97
	10	0	42	65	39

From Tables II and V, it can be concluded that the impregnated filter method is most useful for short-time measurements. Sampling times of one day can be used if the humidity is not too low; if it is low then two filters in series and/or a lower linear air velocity must be used. The same measures can be taken on long-time tests when medium concentrations (more than 0.1 mg/m^3) are to be expected. At high humidities it may be safer to determine the sulfur dioxide as sulfate, instead of as sulfur dioxide if long sampling times (one day or more) are used.

The difficulties encountered in the 1-day measurements are also found in the 10-day measurements, but here they have grown in importance. It is no longer possible to determine the sulfur dioxide as such and the peak and mean concentrations must be even lower or the air velocity slower.

The results of the measurements concerning application (*4*) were as follows: the mean of the absolute deviations from the calculated quantities of sulfur dioxide on the spots through which sulfur dioxide was drawn, was 5.7%, and the deviation of the mean from the calculated mean was 2.7%. No reason was found to suppose that the absorbed sulfur dioxide was not 100% preserved. The mean concentration found on the 464 clean spots was 1 μg/m^3; the mean of the absolute differences between the concentrations found and their mean was 0.2 μg/m^3.

Hardly any indication of contamination of the "clean" spots by the "dirty" spots was found: two clean spots showed concentrations of respectively 66 μg/m^3 and 20 μg/m^3.

The results of some other experiments, mainly about details in the practical application of the method, are discussed below.

Washing of filters. There are two acceptable ways of washing the sulfur dioxide out of the filters. The first is to put the filter on a sintered-glass support and draw the wash liquid through it. The second is to put the filter in a beaker with the wash liquid and wash by shaking or stirring. In the first method the wash solution must not be acidic if accurate results are to be obtained. This excludes the direct use of the *p*-rosaniline reagent. A quantity of 1 ml of wash solution/cm^2 of filter is sufficient; in one experiment only 0.06% of the sulfur dioxide was found in a second wash. In the second method, water containing an amount of acid equivalent to the alkali of the filter may be used; again it is not advisable to use the *p*-rosaniline reagent directly. In both methods, a solution of sodium chloromercurate can be used to increase the permissible time-lapse between washing and analysis. This also makes it possible to use a wash solution containing the neutralizing amount of acid in the first method and the *p*-rosaniline reagent in the second method. It must be noted that triethanolamine binds mercury by complex formation.

Effect of alkali content of filters on p*-rosaniline method.* The optical density obtained for a given quantity of sulfur dioxide in the *p*-rosaniline method depends on the acidity of the final solution; thus if the alkali of the filters is not neutralized exactly, an error arises. If the filters are impregnated to contain 0.07 mmol of potassium hydroxide/cm^2 and an amount of 1 ml of wash solution/cm^2 is used, the amount of alkali is just about equivalent to the amount of acid present in the reagent to be added. If extra neutralizing acid is not added, a high optical density is obtained. However, if the amount of extra acid is double the necessary amount, the quantity of sulfur dioxide found (0.15 μg/cm^2 + 5%) is low. A variation of not more than 10% in the amount of alkali is readily obtainable and the resulting error is acceptable. To be on the safe side, it is advisable to use a somewhat higher final acidity than that normally obtained.

Storage and drying of unused filters. Filters that are not used within a short time after preparation must be stored under such conditions that they do not take up any carbon dioxide; this can be done in a desiccator over silica gel. It was found that the filters did not take up an important amount of carbon dioxide even after eight weeks. Bicarbonate appeared to change back to carbonate under these conditions. When filters were kept as advised and used when still dry, they were slightly less effective than moist filters; efficiencies of respectively 92 and 95% were found at a concentration of 15 mg/m^3 during 1 min at a humidity of 35%.

Effect of linear air velocity. One would expect the effect of, for instance, halving the linear air velocity to be about the same as doubling the concentration or doubling the filter thickness. The results obtained so far are not sufficient in number to allow certainty on this point. Normally our linear air velocity was about 15 cm/sec, but efficiencies of over 99% could be obtained at high humidities at 10 times this rate.

Recovery of known SO_2 concentrations. A known concentration (see EXPERIMENTAL) of about 8 mg of sulfur dioxide/m^3 was determined in 8 replicate determinations by the impregnated filter method. The variation about the mean of the results was 4% and the deviation of the mean from the calculated value was 1.3%, which was slightly better than expected.

Practical use. We have used the filter method for about a year in the field under all sorts of weather conditions, comparing it with the impinger method, mostly in 30-min or 60-min measurements. The sulfur dioxide concentrations measured ranged between 0.02 mg/m^3 and 1 mg/m^3. The mean absolute difference of the values obtained by the two methods was 0.015 mg/m^3 or 6%. The difference in the mean values was 0.01 mg/m^3 or 4%, the filters giving the lowest value. The difference was not significant at the 95% level. A systematic error of 1% may have arisen from the fact that the air flow was dried after the impingers, but before measurement.

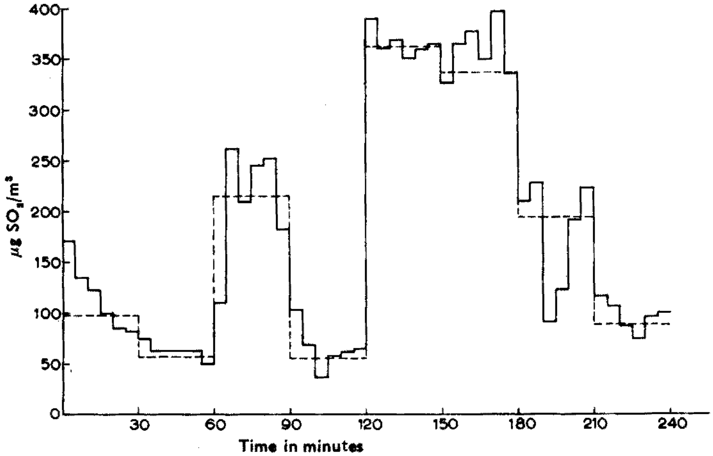

Fig. 4. Comparison between values obtained by automatic sampling (5-min values) and by normal filter method (30-min values).

Fig. 4 shows a comparison between 5-min values obtained with a Gelman automatic filter-tape sampler and 30-min measurements by the new filter method. In Table VI the latter are also compared with the mean 30-min values calculated from the 5-min values. The agreement is satisfactory.

TABLE VI

COMPARISON OF RESULTS BY AUTOMATIC AND NORMAL FILTER METHODS

Mean 30-min SO_2 concentration (mg/m^3)		*Absolute difference*	
Automatic sampler	*Normal filter method*	*($\mu g/m^3$)*	*(%)*
0.116	0.097	19	20
0.062	0.056	6	11
0.210	0.215	5	2
0.065	0.054	11	20
0.366	0.362	4	1
0.326	0.337	11	3
0.177	0.194	17	9
0.093	0.088	5	6
Mean 0.177	0.175	10	9

When the humidity was very high we found that the filters lost strength because of the uptake of water. The danger of splitting the filters can be eliminated by supporting them, by warming the air, by lowering its pressure, or by using two filters on top of each other.

DISCUSSION

The more important conclusions which can be drawn from the present work are as follows.

(*1*) Filter paper impregnated with solutions of potassium hydroxide with added glycerol or triethanolamine has a high sampling efficiency for sulfur dioxide in air provided that the following conditions are fulfilled:

(*a*) relative humidity not lower than 30%,

(*b*) sulfur dioxide concentration not higher than 10 mg/m^3,

(*c*) total quantity of sulfur dioxide collected not more than equivalent to 10% of the alkali of the filter,

(*d*) linear velocity of the air drawn through the filters not more than 15 cm/sec.

One of these limits may be overstepped if the other conditions are adjusted accordingly.

(*2*) If the sampling time is longer than one day, the sulfur dioxide concentration must be lower than 10 mg/m^3 or the air velocity less than 15 cm/sec.

(*3*) Sulfur dioxide absorbed by the filters is very resistant to oxidation if the filters are kept dry.

(*4*) If the sampling time is more than one day, it is safer to determine the sulfur dioxide as sulfate instead of as such.

From these points it is clear that impingers can be replaced by the impregnated filter method. Its application in automatic samplers also merits consideration. Automatic filter-tape air-samplers are commercially available and can be used with impregnated filter tape for the sampling of sulfur dioxide if so modified that the rolls of tape are kept dry. Full advantage of the automatic sampling cannot be taken unless it is followed by automatic analysis; for this purpose we are now trying to construct an automatic analyser that will punch out the sample spots, add wash solution and reagents by means of automatic pipets, measure the optical density of the resulting liquid and print out the concentration of the air pollutant. The latter will be made possible by using a spectrophotometer with automatic compensation of the light absorption by means of a moving wedge. The wedge will be coupled mechanically to a printing rotation counter. A time interval of 30 sec between two analyses is planned. Thus the analyser will be able to keep pace with ten automatic samplers set to take 30-min samples. It might seem that ten samplers taking 5-min samples, in combination with an automatic analyser, will give the equivalent of ten of the commonly used recording air analysers for a much lower price. However, this is not quite true because the recording instruments give the value of the concentration in a much shorter time. On the other hand the filter analyser can give the mean value of the concentration in digital form, which is an advantage if one is interested in, for instance, 30-min values rather than peak values.

The most important limitation of the impregnated filter paper method seems to be the low efficiency at low humidities. It is true, at least in Holland, that an outdoor humidity below 30% is very seldom measured, but when the outdoor temperature is low, the relative humidity may decrease considerable if the air becomes warmer before filtration, for instance, in a mobile laboratory. In such cases, the filter holders must be placed outside or — less good — the air must be humidified before filtration.

There are four factors influencing the collection efficiency: diffusion in the gas phase, adsorption on the liquid surface, chemical reaction with the absorption solution, and diffusion in the liquid phase. The humidity, air velocity, total quantity of sulfur dioxide and its concentration each influence these factors, but it is difficult to determine experimentally the exact effect of each variable. However, the results indicate that diffusion in the gas phase is not a limiting factor, so that it would be more important to use other kinds of impregnating solutions rather than other kinds of filter paper.

Other points still to be investigated are the influence on the collection efficiency and the stability of absorbed sulfur dioxide, of other air pollutants such as oxidants, nitrogen dioxide, hydrogen sulfide and dust (especially iron oxides). However, the usefulness of the method appears to be sufficiently well established to justify publication of the results obtained so far.

SUMMARY

A method is suggested for the sampling of sulfur dioxide in air with impregnated filter paper instead of bubblers. The best aqueous impregnating solution contained potassium hydroxide with glycerol or triethanolamine. The possibilities and limitations of the method are discussed. High collection efficiencies (over 95%) were obtained at relative humidities above 25%. Collected sulfur dioxide was stable for at least several weeks when the filters were kept dry after the sampling. The method is especially suited for short-time measurements and for automatic sampling with smoke samplers.

RÉSUMÉ

Une méthode est proposée pour le prélèvement d'anhydride sulfureux dans l'atmosphère en utilisant du papier à filtrer imprégné. Les meilleurs résultats ont été obtenus avec des solutions aqueuses d'hydroxyde de potassium, additionnées de glycérol ou de triéthanolamine. Cette méthode convient spécialement pour des déterminations de courte durée et pour des prélèvements automatiques.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Entnahme von Luftproben mit Hilfe von imprägniertem Filterpapier. Als Imprägnierflüssigkeiten eignen sich besonders wässrige Kaliumhydroxydlösungen,

die noch Glycerin oder Triäthanolamin enthalten. Anwendungsmöglichkeiten und Grenzen der Methode werden diskutiert. Sie eignet sich besonders für kurzfristige Messungen und für automatische Probeentnahmen in Rauchprüfgeräten.

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POLAROGRAPHY OF URANIUM IN LACTATE MEDIUM

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Polarography of uranium is interesting from the point of view of the disproportionation of uranium(V) formed by reduction of uranium(VI) at the electrode[1-4]. A study of this phenomenon in the presence of certain complexing agents has already been described[5]; the present paper reports the polarography of uranium in lactate medium.

EXPERIMENTAL

Apparatus

Current–potential curves were measured manually on a Cambridge Pen-Recording polarograph at a sensitivity of 1/15 corresponding to 0.5 μA per division. An H-type cell with a saturated calomel electrode (S.C.E.) as the reference electrode was used for the measurements at $30 \pm 0.5°$ with deaerated solutions. The capillary characteristics were: $m = 0.80$ mg sec^{-1} and $t = 4.8$ sec at -0.5 V *vs.* S.C.E. in the supporting electrolyte used.

Chemicals

Reagent grade chemicals were used. The preparation of the uranium solution has been described earlier[5]. Sodium lactate was determined by passing an aliquot of the solution through a column of a cation exchanger (Dowex 50) and titrating the effluent with standard alkali. The ionic strength was maintained at 1.0 by the addition of requisite amounts of sodium perchlorate. Thymol ($1 \cdot 10^{-3}$% in the final solution) was used as the maximum suppressor.

RESULTS AND DISCUSSION

The polarographic behaviour of uranium in lactate medium was studied at different pH values. The behaviour can be roughly divided into three categories: (*1*) at pH 1, the limiting current of the uranium(VI) wave increases by about 50% of the current obtained in the absence of lactate, without any change in the half-wave potential, (*2*) at pH 5, the limiting current is the same as that of the simple ion but there is a shift in the half-wave potential, and (*3*) at pH 6, the half-wave potential shifts to still more negative values and the reduction appears irreversible, while the limiting current remains the same as in (*2*).

(*1*) *pH 1*: Polarograms of uranium were obtained at pH 1.1 ± 0.1 with different amounts of sodium lactate. The pH was adjusted by suitable addition of hydrochloric acid. A typical curve is given in Fig. 1A. The half-wave potential of the uranium(VI) wave is nearly the same as that of the simple ion, and the slope of 63 mV for the log-plot corresponds to a one-electron reversible reduction. The limiting current is higher by about 50% than that obtained in the absence of lactate (Table II). The increase in the current due to the amount of acid only is about two divisions, and any further increase in the current is due to the complex favouring the disproportionation of uranium(V) formed at the electrode. This is verified by studying the effects of the uranium concentration and the temperature on the limiting current.

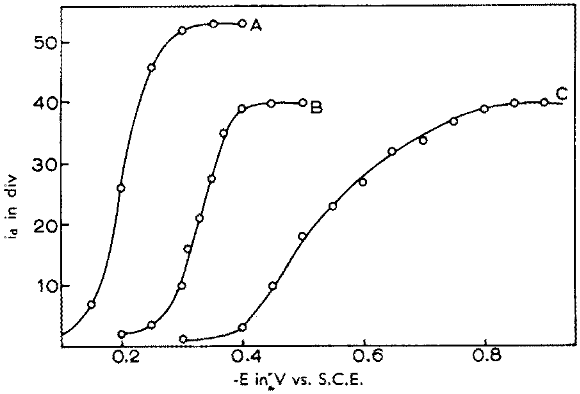

Fig. 1. Polarograms of uranium in lactate medium. A. 1 mM U, 0.67 *M* lactate at pH 1, B. 1 mM U, 0.27 *M* lactate at pH 5, C. 1 mM U, 0.67 *M* lactate at pH 6.

The increase in the ratio, i_l/C with the concentration of uranium (Table I) is understandable, as the fraction of uranium(V) disproportionating becomes greater with increasing uranium concentrations. A high temperature coefficient of 3–4% also indicates an increase in the rate with temperature. These two effects indicate that the lactate complexes favour the disproportionation of uranium(V) at the electrode.

The equations derived by KOUTECKY AND KORYTA[7] for the rate of disproportionation of the depolariser product are

$$\frac{i_l}{i_a} = 1 + \sum_{i=1}^{\infty} C_i \xi^i \tag{1}$$

for which

$$\xi = 2\,akt \tag{2}$$

where i_l and i_a are the maximum limiting and diffusion currents respectively, a is

TABLE I

EFFECT OF URANIUM CONCENTRATION AND TEMPERATURE ON THE LIMITING CURRENT OF URANIUM(VI)

Sodium lactate = 0.67 *M*; pH = 1.1

Concentration of uranium (C) mM	*Temperature °C*	*Limiting current at −0.4 V vs. S.C.E. (i_l) div.*	*i_l/C div./mM*	*Temperature coefficient*[6] *%*
0.2	—	10	50	—
0.5	30	26	52	—
1.0	—	55	55	—
2.0	—	113	56.5	—
—	30	55	—	—
1.0	42.5	90	—	4.0
—	50	100	—	3.0

the initial concentration of the depolariser, and t is the drop time. Values of i_l/i_d can be calculated for assigned values of ξ from a knowledge of the C_t values for i[8].

TABLE II

RATE CONSTANTS FOR THE DISPROPORTIONATION OF URANIUM(V) IN LACTATE MEDIUM

U = $1 \cdot 10^{-3}$ *M*; pH = 1.1

Sodium lactate M	*i_l div.*	*i_l/i_d*	*ξ*	*k mol^{-1} sec^{-1}*
0	39	—	—	—
0.13	43	1.10	1.5	160
0.20	47	1.20	3.45	360
0.27	51	1.31	5.55	580
0.40	53	1.36	6.60	690
0.53	54	1.38	7.00	730
0.67	55	1.41	7.50	780

TABLE III

EFFECT OF LACTATE ON URANIUM(VI) WAVE

U = $1 \cdot 10^{-3}$ *M*; HCl = 0.01 *M*; pH = 5±0.4

Sodium lactate (M)	*$E_{\frac{1}{2}}$ (−V vs. S.C.E.)*	*Limiting current at −0.5 V vs. S.C.E. (div.)*	*Slope (mV)*
0.07	0.279	40	60
0.10	0.296	41	—
0.13	0.304	40	—
0.27	0.332	41	59
0.40	0.345	41	60
0.52	0.361	40	61
0.67	0.370	40	60

The rate of disproportionation of uranium(V) in the lactate medium was calculated using equations 1 and 2. ξ values were calculated for experimental values of i_l/i_d and from these, k, the rate of disproportionation, was calculated (Table II). McEwen and De Vries[8] have calculated the rate of disproportionation in fluoride medium, substituting fluoride/uranium ratios for a, the concentration of the depolariser, in the above method. When lactate/uranium ratios from the above data were used for the purpose of comparison, a rate smaller than that in the fluoride medium was obtained; this may be attributed to the difference in the stability of these complexes.

(2) *pH 5*: A typical polarogram of uranium in this medium at pH 5±0.4 is given in Fig. 1B, and the half-wave potentials at different concentrations of lactate are listed in Table III. The slope for the log-plot is 60±1 mV, indicating a one-electron reversible reduction. The half-wave potentials also shifted to more negative potentials, indicating complex formation of uranium with lactate.

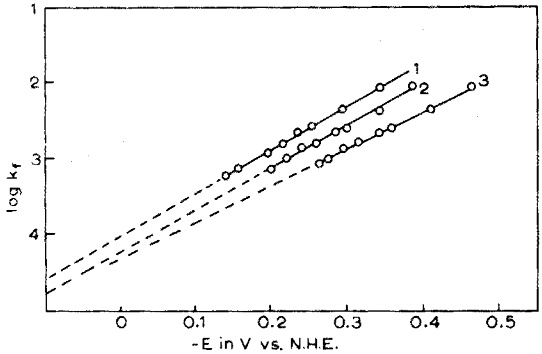

Fig. 2. Plot of E *vs.* log k_f. (1) 1 mM U + 0.133 M sodium lactate, pH 5.9, (2) 1 mM U + 0.399 M sodium lactate, pH 6, (3) 1 mM U + 0.665 M sodium lactate, pH 6.2.

The limiting current of 40 divisions is the same as that of the simple ion. The proportionality between current and concentration of uranium and the temperature coefficient (Table IV) of less than 2% indicates that a complex is reduced at the electrode and that no kinetic considerations are involved.

(3) *pH 6*: A polarogram of uranium(VI) at pH 6 (Fig. 1C) was found to be highly irreversible (Table V). The limiting current is the same, indicating a one-electron reduction. The rate constants for the irreversible electrode reaction were calculated by Koutecky's[9,10] method using the following equations:

$$\frac{i_l}{i_d} = F(\chi) - \xi^* Hc(\chi) \tag{3}$$

for which

$$\xi^* = 50.4\, D^{1/2} m^{-1/3} t^{1/6} \tag{4}$$

and

$$\chi = k_f (12t/7D)^{1/2} \tag{5}$$

(assuming k_b to be small for an irreversible process); the other symbols have their usual significance. The rate constant, k_f, for the forward reaction of a cathodic process varies with the electrode potential E as follows:

$$k_f = k_f^\circ \exp(-\alpha nFE/RT) \tag{6}$$

where α is the transfer coefficient, n is the number of electrons involved in the rate-determining step, and k_f° is the rate constant of the electrode process at 0 V *vs.* N.H.E. From the above equations, a plot of log k_f *vs.* E (Fig. 2) was obtained. Good straight lines were obtained, from the slopes of which the values of αn were calculated. Extrapolation to 0 V and +0.05 V (half-wave potential of UO_2^{2+}) gave the values of k_f° and k_s respectively (Table V).

The polarograms observed at pH 5 and 6 can be interpreted on the basis of complexation of UO_2^{2+} and of the acid concentration being too low to favour disproportionation. This was verified from a study of the effects of temperature and concentration of uranium on the limiting current. The reduction waves at pH 5 and 6 could be explained on the basis of different species existing in solution. FELDMAN *et al.* in their spectrophotometric studies on the uranium–lactate system suggest the formation of a 1:1 complex at pH 3.5[11] and formation of a trimer at pH 6[12].

TABLE IV

EFFECTS OF URANIUM CONCENTRATION AND TEMPERATURE ON THE LIMITING CURRENT OF URANIUM(VI) AT PH 5

Uranium (C) mM	*Temperature °C*	*Limiting current (i_l)div.*	*i_l/C div./mM*	*Temperature coefficient %*
0.5	—	20	40	—
1.0	30	40	40	—
2.0	—	81	40.5	—
1.0	30	40	—	—
—	42	50	—	1.6
—	52	60	—	1.9

TABLE V

RATE CONSTANTS FOR THE REDUCTION OF URANIUM(VI) AT PH 6

Sodium lactate M	αn	k_s *cm/sec*	k_f° *cm/sec*
0.13	0.33	$10^{-4.3}$	$10^{-4.0}$
0.40	0.33	$10^{-4.5}$	$10^{-4.0}$
0.67	0.30	$10^{-4.5}$	$10^{-4.3}$

The authors wish to thank Dr. V. T. ATHAVALE, Head of the Analytical Division, for his interest and encouragement, and V. S. SRINIVASAN for helpful discussions.

SUMMARY

The polarography of uranium(VI) in the lactate medium is studied at different pH values. At pH 1 the half-wave potential of the uranium(VI) wave remains the same as that of the simple ion, but the limiting current increases with increasing concentration of lactate; disproportionation of uranium(V) at the electrode surface is suggested. The rate of disproportionation is calculated. Polarograms observed in the region of pH 5 and 6 are interpreted on the basis of complexation of UO_2^{2+}.

RÉSUMÉ

Les auteurs ont étudié le comportement polarographique de l'uranium(VI), en milieu lactique, à différents pH. Au pH 1 le potentiel de demi-vague de l'uranium(VI) reste le même que celui de l'ion simple; mais le courant limite croît avec l'augmentation de la concentration du lactate. Une explication est donnée. Les polarogrammes examinés aux pH 5 et 6 sont interprétés sur la base d'une complexation de UO_2^{2+}.

ZUSAMMENFASSUNG

Das polarographische Verhalten von Uran-(VI) in Laktat-Medium bei verschiedenem pH wurde untersucht. Bei pH 1 bleibt das „half-wave" Potential des Uran-(VI) das gleiche wie für das einfache Ion, aber der Grenzstrom nimmt zu mit zunehmender Konzentration an Laktat. Es wird angenommen, dass eine Disproportionierung des Uran-(V) auf der Elektrodenoberfläche stattfindet. Der Grad der Disproportionierung wurde berechnet. Polarogramme im Gebiet von pH 5 und 6 werden durch Komplexierung des UO_2^{2+} erklärt.

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ANALYTICAL APPLICATIONS OF INFRA-RED SPECTROSCOPY

THE BEHAVIOUR OF THE OXINATES OF NIOBIUM, TANTALUM AND ASSOCIATED ELEMENTS

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Investigations carried out on reduction systems for niobium and tantalum have shown[1] that niobium can be determined colorimetrically in the presence of tantalum, but that titanium and, to a lesser extent, vanadium and tungsten always cause trouble. To overcome this difficulty the possibilities of infra-red spectroscopy using the potassium bromide disc technique were investigated. This technique[2,3] had proved to be very successful in problems of a similar nature in earlier work.

It appeared necessary to choose complexes of niobium which are readily formed, of known composition, and possessing an oxygen bridge between metal and ligand. All these characteristics appeared to be satisfied by the 8-hydroxyquinoline complexes of these metals, which were therefore chosen. The method developed is based on the precipitation of the metal oxinates. The filtered precipitate is dried, mixed and pressed with potassium bromide into a disc, and examined in the infra-red spectrophotometer.

PRELIMINARY INVESTIGATIONS

Niobium when complexed with 8-hydroxyquinoline gives an infra-red spectrum which is basically the same as that of oxine itself, but certain important differences appear. The principal difference is the appearance of a peak at 10.85 μ which is characteristic of the Nb—O group[4]. The peak is sharp in contrast to the broad adsorption band obtained for this grouping in the spectra of inorganic salts. The spectra of 8-hydroxyquinoline and the niobium complex are shown in Figs. 1 and 2. Tantalum exhibits a similar behaviour, the oxinate showing peaks in the infra-red region at 10.94 μ, 11.06 μ, and 14.05 μ (Fig. 3). The peak at 10.94 μ interferes with that of niobium at 10.85 μ, but there is no interference from the tantalum peak at 11.06 μ. The technique thus offers the basis of an analytical method for the determination of niobium and tantalum. By determining the tantalum at 11.06 μ a correction can be applied for the contribution at 10.85 μ, thus permitting the determination of niobium.

Other elements which might be expected to be present with niobium and tantalum in alloys were also investigated. Titanium (Fig. 4), zirconium, hafnium, aluminium, gallium, indium, thallium, thorium and iron show no characteristic absorption peaks presumably because of the absence of the metal-oxygen grouping in the oxinate.

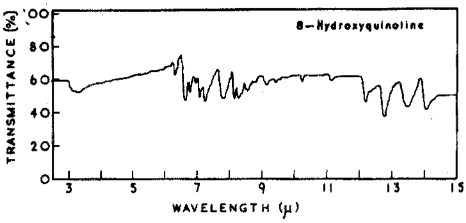

Fig. 1. Infra-red absorption spectrum of 8-hydroxyquinoline.

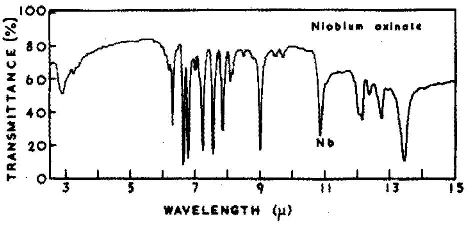

Fig. 2. Infra-red absorption spectrum of niobium oxinate.

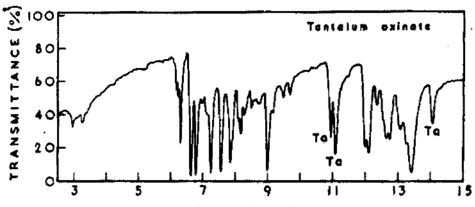

Fig. 3. Infra-red absorption spectrum of tantalum oxinate.

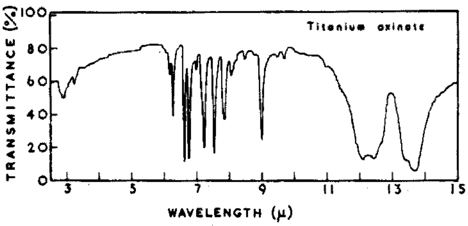

Fig. 4. Infra-red absorption spectrum of titanium oxinate.

Metals which do show absorption peaks are tungsten, molybdenum, vanadium, manganese and cobalt. A summary of the important peaks in the infra-red shown by the oxinates of these metals is given in Table I.

TABLE I

Metal	*Peaks (μ)*		
W	10.58	10.87	11.08
Mo	10.79	10.91	11.11
V	10.40	14	(a broad band)
Mn	11.06		
Co	10.96		

It is clear from Table I that vanadium is the only metal which does not interfere with the determination of niobium and tantalum. Vanadium can be determined in a mixture of all three elements. Tungsten or molybdenum may be determined in the presence of niobium or tantalum, and a correction applied using the peaks at 10.58 μ or 10.79 μ. Niobium may be determined in the presence of tungsten or tantalum, but the presence of both these elements except in very small amounts must be avoided. In view of the above experiments it was considered more practical to eliminate as many as possible of the interfering elements before the final oxinate precipitation.

The results obtained as outlined above were used to develop a procedure for the determination of niobium and tantalum in the presence of one another, and an attempt was made to apply the method to the determination of these two elements in steels. The perchloric acid method[5] was used to precipitate niobium and tantalum; after this treatment only tungsten of the interfering elements would be present.

EXPERIMENTAL

Apparatus

The infra-red spectra were recorded on a Perkin Elmer ('Infracord') Spectrophotometer, Model 137. Potassium bromide discs were prepared with a Perkin Elmer die using an 'Apex' hydraulic press with a 10-ton capacity on a ram of $2^1/_8$ inch diameter. Before use the potassium bromide was dried at 150° for 24 h.

Procedure

Dissolve about 0.2 g of the niobium–tantalum alloy in 50 ml of 1 : 1 hydrochloric–nitric acid mixture. Add 35 ml of 71% perchloric acid and heat until the acid begins to boil. Cover and reflux for 30 min. Cool and add 50 ml of distilled water, 50 ml of sulphurous acid solution and a small quantity of paper pulp. Dilute to 300 ml with distilled water. Stir and boil gently for 10 min, then digest for 2 h. Cool, filter through No. 40 Whatman filter paper, and wash thoroughly with 2% hydrochloric acid. Ignite the precipitate. Fuse the precipitate with potassium pyrosulphate and dissolve the melt in 5 ml of 1 *M* oxalic acid. Add 0.5 ml of concentrated sulphuric acid and 50 mg of 8-hydroxyquinoline. Heat to boiling and add 3 g of urea. Dilute to 100 ml. Leave on a water bath until the solution turns brown. The pH should be maintained between 7 and 8. Filter through a sintered glass crucible, wash thoroughly with water, alcohol and ether, dry in an oven at 140° and weigh.

Grind a representative sample of the precipitate (2 mg) with 200 mg of potassium bromide in an agate mortar to a homogeneous form. Transfer the finely-divided mixture to the die and form into an even layer with the plunger. Replace the plunger of the die and evacuate for 2 min. Apply a total pressure of 10 tons for 5 min. Fix the disc into a suitable holder and place in the sample beam of the 'Infracord', using a pure potassium bromide disc of similar weight in the reference beam. Record the spectrum over the range 9–15 μ.

To calculate the optical density a base-line technique[3] was used. Draw a line at the base of the band and calculate the optical density from the incident (I_0) and transmitted (I_t) intensities.

At the conclusion of the experiment, re-weigh the disc and correct the amount of oxinate to 200 mg total disc weight.

The concentrations of niobium and tantalum are determined from standard calibration curves of optical density against concentration.

Notes

(*1*) The method of urea hydrolysis[6] is the only means of obtaining complete precipitation of the oxinates of niobium and tantalum.

(*2*) Care must be taken in preparing the disc to ensure that the grinding is as fine as possible, and that the oxinate–bromide mixture is completely homogeneous.

(*3*) In the pressing of the disc the thickness should be uniform throughout.

(*4*) In calculating the weight of niobium from the weight of oxinate the formula $NbO(C_9H_6ON)_3$ was used, thus 1 g of niobium oxinate corresponds to 0.1719 g Nb. For tantalum the corresponding formula was used, thus 1 g of tantalum oxinate corresponds to 0.2872 g Ta.

(*5*) The calibration curve for niobium oxinate is linear over the range 0–2.0 mg of niobium oxinate at 10.85 μ, the optical density ranging from 0 to 1.25. The curves for tantalum oxinate at different wavelengths are shown in Fig. 5.

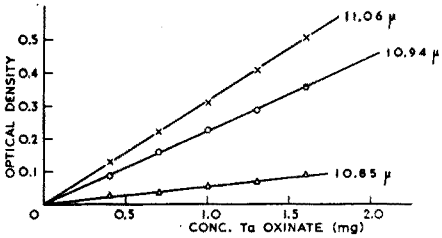

Fig. 5. Calibration curves for tantalum oxinate at three wavelengths (1 g tantalum oxinate ≡ 0.2872 g tantalum).

DISCUSSION AND RESULTS

It can be seen from Fig. 6 that the tantalum peak at 10.94 μ interferes with the niobium peak at 10.85 μ. The tantalum absorbance at this wavelength changes rapidly and it is not possible to read it directly. It is assumed, however, that the absorbance of tantalum between 10.80 μ and 10.94 μ is linear; from the spectra this is a reasonable assumption. The optical density of tantalum at 10.85 μ for various concentrations can therefore be determined. Further, since the tantalum concentration can be determined without interference from the peak at 11.06 μ, the tantalum influence on the optical density for niobium at 10.85 μ can be calculated and both elements determined. Vanadium may also be determined if present in the mixture, from its peak at 10.40 μ.

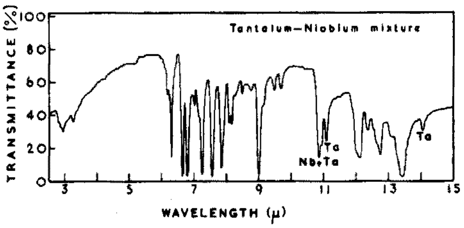

Fig. 6. Absorption spectrum of niobium oxinate–tantalum oxinate mixture.

In the absence of vanadium, tungsten may be determined in the presence of niobium and tantalum using the peak at 10.58 μ. The tantalum peak at 14.05 μ is thought to be due to a Ta—O—Ta type of linkage, probably arising from polymerisation of the oxinate complex. This peak is not reproducible even under rigid experimental conditions and therefore is not analytically important. The tantalum peaks at 10.94 μ and 11.06 μ are probably due to the Ta—O linkage.

Synthetic mixtures of 'unknown' composition and a standard niobium–tantalum steel were analysed by one of us. The results are shown in Table II.

Tantalum was present in the sample of steel but in too small a concentration for its accurate determination; 0.2 mg of tantalum oxinate per 200 mg disc was the smallest amount which could be accurately determined. The background absorption over the complete spectrum range increased with the total oxinate concentration, so that at concentrations greatly in excess of 2 mg per 200 mg disc it became high enough to lower the transmittance readings at the niobium and tantalum maxima to below 15%; in this region Beer's law was no longer strictly obeyed. This imposes a limitation on the method, in that the niobium : tantalum ratio cannot be allowed to exceed 10 : 1; thus in the above case tantalum could not be determined accurately by extending the method to cope with larger samples.

TABLE II

ANALYSIS OF 'UNKNOWN' MIXTURES

No.	*Nb (mg)*		*Ta (mg)*	
	Found	*Present*	*Found*	*Present*
1	4.95	5.00	4.7	5.00
2	2.9	3.00	5.7	6.00
3	5.8	6.00	3.0	2.80

Analysis of Nb/Ta steel (B.C.S. sample)

Steel —	Actual composition	Nb + Ta	0.71%
	Found	Nb	0.65%
		Ta	0.06%

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SUMMARY

The behaviour of the oxinates of niobium, tantalum and associated metals in the infra-red region was studied and a method developed for the determination of niobium and tantalum. Vanadium caused no interference, but other heavy metals, such as molybdenum, manganese and cobalt, which interfered were removed by preliminary treatment when the method was applied to the determination of niobium and tantalum in steels.

RÉSUMÉ

Les auteurs ont examiné le comportement des oxinates de niobium, de tantale et de leurs métaux associés, en spectroscopie infra-rouge. Une méthode a été mise au point pour le dosage du niobium et du tantale. Le vanadium ne gène pas; mais d'autres métaux lourds (Mo, Mn, Co) doivent être séparés au préalable.

ZUSAMMENFASSUNG

Das Verhalten der Oxinate von Niob, Tantal und Begleitmetallen im Infra-rot Gebiet wurde untersucht und eine Methode entwickelt zur Bestimmung von Niob und Tantal. Vanadium stört nicht, aber andere Schwermetalle wie Molybdän, Mangan und Kobalt stören und müssen vorher entfernt werden, falls die Methode zur Bestimmung von Niob und Tantal in Stählen angewandt wird.

ANION-EXCHANGE SEPARATION OF HYDROXY ACIDS IN ACETATE MEDIUM

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Chromatographic separations by means of anion-exchange resins are of interest for the separation of hydroxy acids formed during the degradation of cellulose and hemicellulose in various technical processes. In earlier papers it has been demonstrated that elution with borate solution is a useful method for isolating aldonic acids[1] and saccharinic acids[2]. Lactic and glycolic acids can be separated from various saccharinic acids, but the separation of these acids from each other is less effective in this medium[3]. In the present work it is shown that separation in acetate medium is a valuable complement to separation in borate medium when mixtures containing hydroxy acids with only one or two hydroxyl groups are to be analyzed.

EXPERIMENTAL

Reagents

α,β-Dihydroxybutyric (4-deoxy-threonic) acid was prepared by oxidation of crotonic acid with permanganate as described by GLATTFELD AND WOODRUFF[4]. α,γ-Dihydroxybutyric (3-deoxy-glycero-tetronic) acid was synthesized as described by GLATTFELD AND SANDER[5]. Formic, glycolic, lactic, and glyceric acids were obtained from commercial sources (CP or purum grades). The other hydroxy acids were the same as those studied in earlier papers[2,6].

Procedure

All experiments were carried out in a column with an inner diameter of 10 mm. The length of the resin bed was 810 mm. The resin (Dowex 1 X-8) was fractionated in the apparatus of SIMONSON (*cf.*[7]) to obtain a particle diameter of 40–80 μ. The column was conditioned with the eluant to be used in the subsequent elution.

An aqueous solution of the acids to be investigated was neutralized with sodium hydroxide and kept for at least 24 h at pH 10 to split up lactones.

The sample solution containing 9–55 mg of hydroxy acids was introduced with a syringe and the eluant fed at constant flow rate of 0.76 ml/cm²/min using an all-glass pump[7]. The eluate was collected using a time-actuated fraction collector. The temperature in the room was kept at 23 ± 1°. The fractions were analyzed by means of a Technicon AutoAnalyzer using a method described in a previous paper[8]. In the chromatograms the deviation on the strip record was plotted against the eluate volume. The yields were calculated using a calibration curve based upon analyses of known amounts of the acids.

RESULTS AND DISCUSSION

When hydroxy acids which can yield lactones are involved, it is recommended to carry out the ion-exchange separation in media where no lactone formation can occur[1]. Although it is possible to separate glycolic and lactic acids by elution with acid[9], this method cannot be recommended when, besides these acids, also hydroxy acids which give rise to interfering lactone formation are present. In the present work sodium acetate solution was chosen as eluant. It should be emphasized that it is very important that lactones present in the sample solution be saponified quantitatively before the sample is introduced into the column. Otherwise, an elution band corresponding to the lactone is obtained. During its passage through the column the lactone can be decomposed and for this reason the lactone band has a long trailing edge.

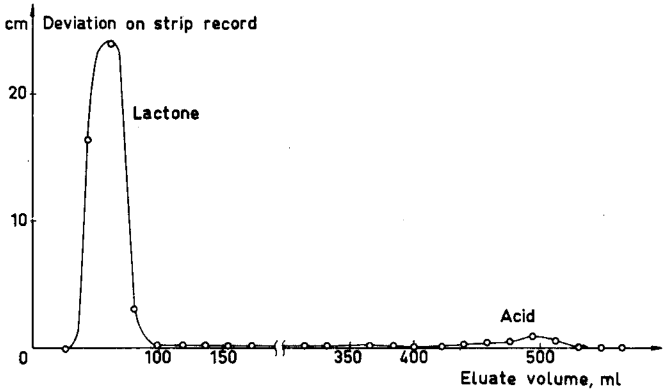

Fig. 1. Elution of α,γ-dihydroxybutyric acid without saponification of lactones. Eluant: 0.15 *M* sodium acetate.

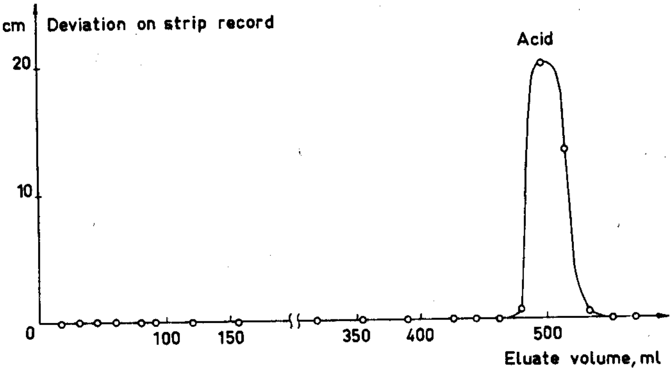

Fig. 2. Elution of α,γ-dihydroxybutyric acid after saponification of lactones. Eluant: 0.15 *M* sodium acetate.

A typical elution curve obtained with a mixture of α,γ-dihydroxybutyric acid and its lactone is given in Fig. 1. After saponification with sodium hydroxide, one distinct elution band is obtained (Fig. 2).

The influence of the eluant concentration upon the separation of glycolic and lactic

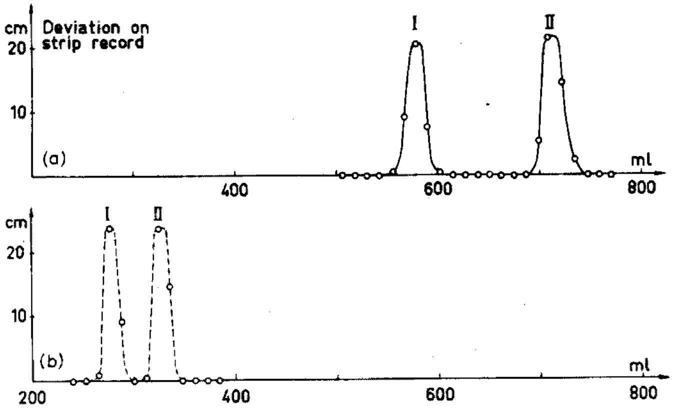

Fig. 3. Separation of lactic(I) and glycolic(II) acids at two different eluant concentrations.

(*a*) 0.15 *M* sodium acetate

	Added (mg)	*Found (mg)*
Lactic acid	12.4	12.5
Glycolic acid	10.4	10.5

(*b*) 0.35 *M* sodium acetate

	Added (mg)	*Found (mg)*
Lactic acid	12.4	12.2
Glycolic acid	10.4	10.3

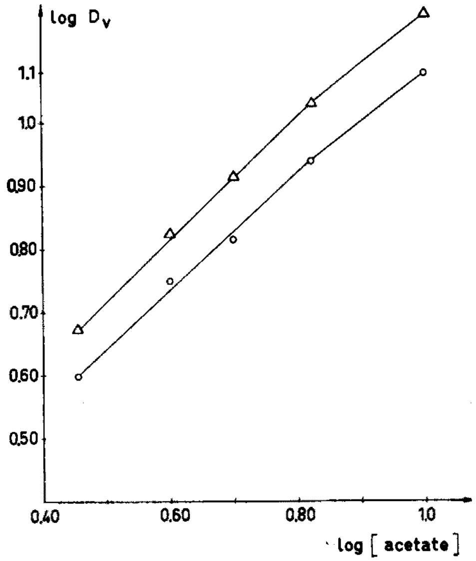

Fig. 4. Influence of the sodium acetate concentration upon the volume distribution coefficient, D_v.

△ Glycolic acid (Slope of straight line: 0.98)
○ Lactic acid (Slope of straight line: 0.94).

acids was studied systematically. The results presented in Fig. 3 show that an excellent separation is obtained over a wide range of concentration. It is evident that when only these two acids are involved, the separation is also quantitative in a much shorter column provided that the lower eluant concentration is chosen.

From these and other experiments the volume distribution coefficient (D_v) and the height of a theoretical plate (Δ) were calculated according to the plate theory (*cf.*[7]). In Fig. 4 log D_v is plotted against the logarithm of eluant concentration. As can be predicted theoretically (*cf.*[7]), the curves can be approximated by straight lines.

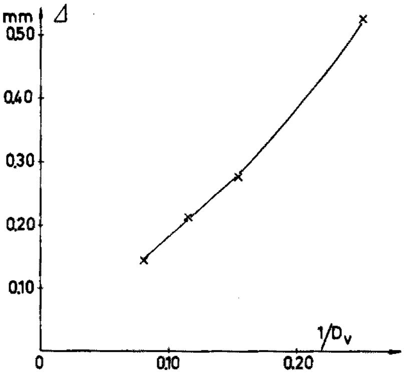

Fig. 5. Correlation between the height of a theoretical plate, Δ, and the volume distribution coefficient, D_v. Calculations based upon experiments with lactic acid.

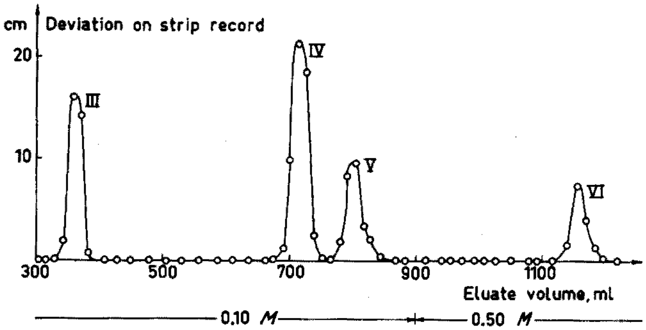

Fig. 6. Separation of various acids by elution with 0.10 M and 0.50 M sodium acetate.

III.	α-D-glucosaccharinic acid
IV.	α,γ-dihydroxybutyric acid
V.	glyceric acid
VI.	formic acid.

The slopes deviate slightly from each other and from unity. The results given in the figure show that the separation factor, *i.e.* the ratio between the distribution coefficients, improves only slightly when the eluant concentration is decreased.

However, the elution curves (Fig. 3) show that a markedly improved separation is obtained at a decreased concentration. This can, according to GLUECKAUF's theory[10], be explained by a decrease in the height of a theoretical plate. The height of a theoretical plate, Δ, was calculated from the width of the elution curves (β). The correlation between eluate concentration and the values recorded by the AutoAnalyzer is not linear and, by means of the calibration curve, the values were recalculated to obtain eluate concentration *vs.* eluate volume. In Fig. 5 the Δ-values obtained with lactic acid at various concentrations of sodium acetate are plotted against $1/D_V$. In most other experiments the elution bands were divided into too few fractions to permit an accurate calculation of Δ. It is seen that Δ increases rapidly for an increase in $1/D_V$. The curve can be approximated by a straight line. The results indicate that diffusion inside the resin particles is the rate-determining step and has a predominant influence upon the height of a theoretical plate.

Various hydroxy acids were studied in experiments with one acid in each run in order to determine the volume distribution coefficients and to study the column behavior of the acids. The eluant concentration was 0.15 *M* in all experiments. Symmetrical or almost symmetrical curves were obtained. The peak elution volumes and the volume distribution coefficients are given in Table I. Results obtained with formic acid are also included in the Table. With formic acid, which is eluted much later than the hydroxy acids, an excessive broadening of the elution band is obtained at the eluant concentration used in these experiments.

TABLE I

PEAK ELUTION VOLUMES ($\bar{v}$) AND VOLUME DISTRIBUTION COEFFICIENTS IN 0.15 *M* SODIUM ACETATE

Acid	$\bar{v}$*(ml)*	D_V
formic	1430	22.1
glycolic	720	10.9
lactic	580	8.7
glyceric	560	8.4
α,β-dihydroxybutyric	490	7.4
α,γ-dihydroxybutyric	500	7.5
α,β-dihydroxyisobutyric	450	6.7
β,γ-dihydroxybutyric	430	6.4
3-deoxy-threo-pentonic	390	5.7
β-D-glucometasaccharinic	330	4.8
α-D-glucometasaccharinic	300	4.3
α-D-glucosaccharinic	270	3.9
α-D-isosaccharinic	250	3.1

With solutions which, besides hydroxy acids, contain formic acid or other acids which are strongly held by the resin, it is advisable to carry out a stepwise elution (or gradient elution) with sodium acetate solution of increasing strength. A separation based upon stepwise elution is demonstrated in Fig. 6. It is seen that the hydroxy acids appear as discrete bands and that formic acid is obtained without excessive tailing.

An almost complete separation of the epimeric forms of glucometasaccharinic acid (Fig. 7) can be easily carried out in 0.08 *M* sodium acetate solution. Similarly, separation of α,β-dihydroxybutyric and α,γ-dihydroxybutyric acids can be carried out provided that the eluant concentration is not too high (Fig. 8). In both separations the width of the elution curves is moderate, which means that an increased column length can be used if it is desired to obtain a quantitative separation (*cf.*[7]).

Separation of a more complicated mixture containing seven hydroxy acids is demonstrated in Fig. 9. Most acids were obtained as well separated bands. The overlapping between the bands corresponding to 3-deoxy-threo-pentonic acid and β, γ-dihydroxybutyric acid is at least partly due to small impurities.

The results obtained in the present work show that when certain hydroxy acids are

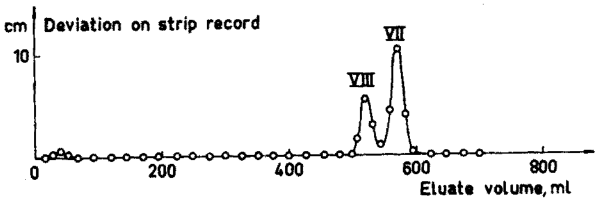

Fig. 7. Separation of glucometasaccharinic acids by elution with 0.08 *M* sodium acetate.

VII. β-D-glucometasaccharinic acid
VIII. α-D-glucometasaccharinic acid.

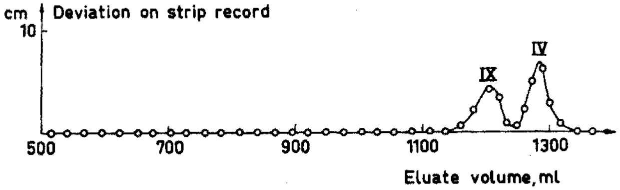

Fig. 8. Separation of dihydroxybutyric acids by elution with 0.06 *M* sodium acetate.

IX. α,β-dihydroxybutyric acid
IV. α,γ-dihydroxybutyric acid.

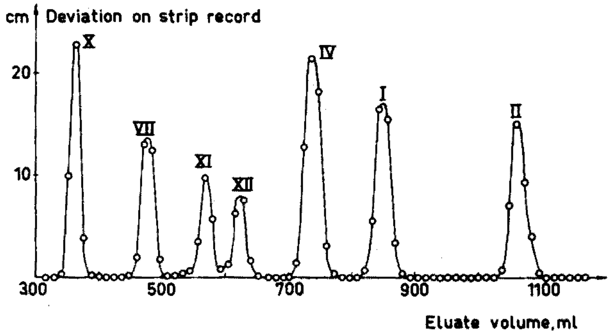

Fig. 9. Separation of various hydroxy acids by elution with 0.10 *M* sodium acetate.

X. α-D-isosaccharinic acid
VII. β-D-glucometasaccharinic acid
XI. 3-deoxy-threo-pentonic acid
XII. β,γ-dihydroxybutyric acid
IV. α,γ-dihydroxybutyric acid
I. lactic acid
II. glycolic acid.

involved, separation is more efficient in acetate medium than in borate medium. In sodium acetate solution the distribution coefficients are chiefly determined by the ion-exchange affinities of the anions present in the solution, whereas in borate medium the distribution coefficient is determined by two main factors: (*a*) ion-exchange affinity, and (*b*) strength of the borate complexes. As can be seen from Table I, the hydroxy acids of a higher molecular weight are eluted ahead of those with a lower molecular weight in acetate medium. Consequently, the ion-exchange affinities increase for a decreased molecular weight. On the other hand, hydroxy acids containing a large number of hydroxyl groups give stronger borate complexes and are eluted after the lower hydroxy acids in borate medium. In many systems the two main factors which determine the distribution coefficient in borate medium will, therefore, counteract each other, which can be a serious disadvantage. With hydroxy acids, such as aldonic acids, containing 5 or 4 hydroxyl groups, complex formation will be the predominant factor in borate medium, whereas with hydroxy acids containing only one or two hydroxyl groups the ion-exchange affinity is the predominant factor.

The financial support of the Swedish Technical Research Council is gratefully acknowledged.

SUMMARY

A great number of hydroxy acids have been separated in an anion-exchange column using sodium acetate as eluant. It is essential that lactones be saponified before loading the column. With hydroxy acids containing only one or two hydroxyl groups this method is superior to separations in borate medium. With complicated mixtures the methods supplement each other.

RÉSUMÉ

Un grand nombre d'hydroxy-acides ont été séparés sur colonne échangeur d'anions, en utilisant l'acétate de sodium comme éluant. Il est essentiel de saponifier les lactones avant de charger la colonne. Cette méthode est supérieure aux séparations en milieu borique dans le cas d'hydroxy-acides renfermant seulement 1 ou 2 groupes hydroxyles. Avec des mélanges compliqués, les deux méthodes se complètent.

ZUSAMMENFASSUNG

Eine grössere Anzahl Oxysäuren wurden mit einer Anionen-Austauscherkolonne und Natriumacetat als Eluierungsmittel getrennt. Laktone müssen vorher verseift werden. Oxysäuren mit einer oder 2 Hydroxylgruppen lassen sich nach dieser Methode besser trennen als nach der Boratmethode. Für die Trennung komplizierter Gemischen werden beide Methoden suppliert.

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LA SÉPARATION Lu–Yb–Tm SUR ÉCHANGEUR DE CATIONS PAR L' α-IHBA

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Plusieurs auteurs[1-4] ont utilisé l'α-hydroxy-isobutyrate d'ammonium (α-IHBA) comme éluant complexant pour la séparation de traces des terres rares sur échangeur de cations. Cet éluant possède en effet un facteur de séparation plus favorable que l'acide lactique et offre en outre l'avantage de permettre de travailler à basse température. Il semblait intéressant de tenter une séparation de macro-quantités des lanthanides Lu, Yb et Tm à température ambiante et à faible concentration de α-IHBA. Une séparation à faible concentration de α-IHBA et à pH élevé est en effet plus économique qu'à forte concentration de α-IHBA et à pH peu élevé.

PARTIE EXPÉRIMENTALE

Réactifs

(*1*) Solution 0.1 *M* d'α-IHBA neutralisée par l'ammoniaque.

(*2*) Echangeur de cations Dowex 50-WX8, 200–400 mesh. L'échangeur est lavé par HCl 6 *M*, eau distillée, NH_3 6 *M*, eau distillée et ensuite débarrassé des gaz dissous par ébullition sous vide dans l'eau distillée.

(*3*) Terres rares. Sesquioxydes Lu_2O_3, Yb_2O_3 et Tm_2O_3 („Specpure", Johnson Matthey) dissous dans l'acide nitrique 14 *N*, évaporés à sec et dissous dans l'eau distillée afin d'obtenir une solution contenant 0.5 mg/ml. Les traceurs radioactifs ^{177}Lu, ^{169}Yb, ^{175}Yb et ^{170}Tm sont préparés en irradiant 100 μl de la solution dans le BR-1 à un flux de 10^{12} neutrons/cm^2/sec, durant 8 h à 1 semaine. Les solutions d'entraineur contenant 10 mg/ml sont préparées de façon analogue.

Appareillage

Colonne. Tube en verre avec diamètre 3 mm, hauteur 30 cm, pourvu d'un manteau thermostatique. La colonne est reliée à une spirale en verre placée en dessous du détecteur à scintillation. Le volume élué est mesuré par comptage électronique des gouttes receuillies dans un collecteur de fractions.

Comptage. L'élution des traceurs est suivie directement par le détecteur à scintillation (crystal NaI(Tl) $1\frac{1}{2}'' \times 1^1/_4''$) relié à un dérivateur et un enregistreur. Chaque goutte donne lieu à une impulsion sur la courbe enregistrée ce qui permet le repère du volume élué. Les fractions collectées peuvent d'autre part être comptées manuellement.

Technique

La colonne de résine, hauteur 15–25 cm, est conditionnée durant une nuit par l'éluant à une température de 25°. Les terres rares, entraineur et traceur (activité ± $2 \cdot 10^5$ c/m) dissoutes dans environ 100 μl d'eau sont introduites au sommet de la colonne et éluées à une vitesse de 8 à 12 sec/goutte *c. à. d.* 1 à 0.6 ml/cm^2/min.

RÉSULTATS ET DISCUSSION

(1) Séparation Lu–Yb–Tm à pH constant

Une séparation de 1 mg des terres rares Lu–Yb–Tm, effectuée à pH = 3.83 sur une colonne de 21.5 cm, à une vitesse d'élution de 1 goutte par 11 sec est représentée dans la Fig. 1. Il apparait que la séparation est excellente, le rapport pic–vallée pour le Lu–Yb étant de 40 (contamination *ca.* 0.9%) tandis que la séparation Yb/Tm est quantitative. L'activité reste en effet égale au bruit de fond durant 11 volumes libres.

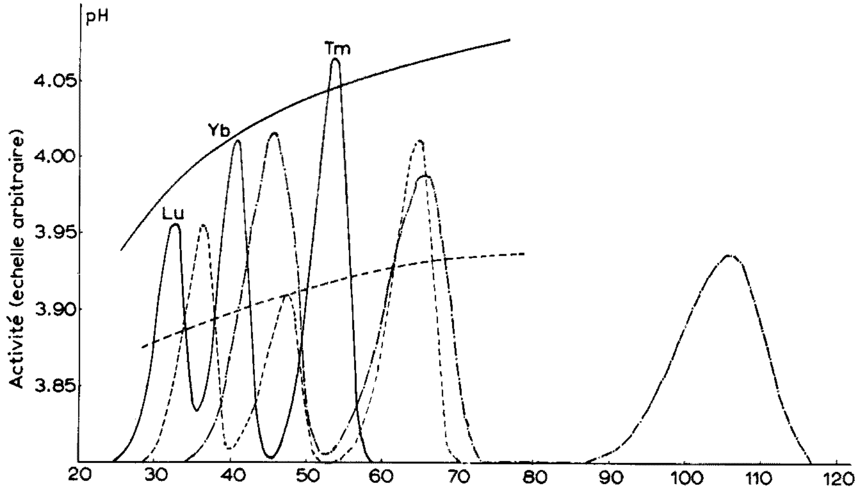

Fig. 1. Séparation de Lu, Yb, Tm. –·–·– pH constant 3.83, – – – pH 3.80–4.05, —— pH 3.79–4.24

(2) Influence de l'entraineur sur la constante de distribution

Les constantes de distribution, K_D, calculées à partir des expériences sur colonnes ne correspondent pas à celles déterminées par DEELSTRA[5] pour les séparations sans entraineur. On a pu démontrer, à partir d'une série de séparations avec des quantités croissantes d'entraineur, que les constantes de distribution sur colonne augmentent en fonction de la quantité d'entraineur (Fig. 2) et que les pics d'élution deviennent plus asymétriques dans la partie ascendante des courbes. Il semble donc que l'augmentation des valeurs de K_D et l'asymétrie des pics soient dues à la faible vitesse d'équilibre entre les différents complexes du type $M^{3+} \rightleftarrows MX^{2+} \rightleftarrows MX_2^{+} \rightleftarrows MX_3 \rightleftarrows MX_4^{-}$.

L'expérience a montré que ces inconvénients ne disparaissent pas en opérant à une température plus élevée. La séparation de macro-quantités des terres rares lourdes à faible concentration de l'α-IHBA et pH élevé n'est donc utilisable que pour des rapports terres rares $M^A/M^{A+1} \leqslant 1$. Afin de pouvoir prévoir la position d'élution, la quantité mise en oeuvre doit d'autre part être connue.

(3) Séparation avec gradient de pH

Le Fig. 1 montre qu'une excellente séparation Lu/Yb/Tm peut être obtenue avec un éluant 0.1 *M* d'α-IHBA et à pH élevé. Le temps requis pour une telle séparation est cependant assez long, notamment d'environ 23 h. La durée de la séparation peut être sensiblement diminuée en faisant appel à un gradient de concentration des ions d'hydrogène ou de complexant.

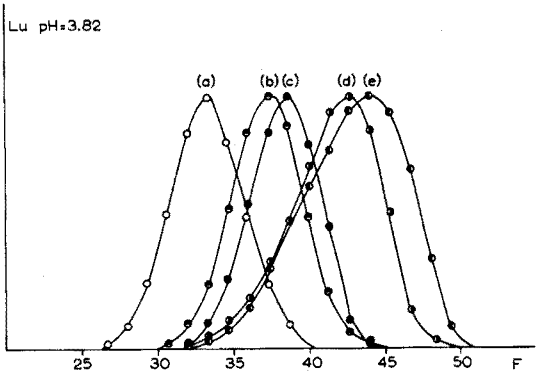

Fig. 2. Effet de la quantité d'entraineur. (*a*) 0.001 mg, (*b*) 0.05 mg, (*c*) 0.1 mg, (*d*) 0.5 mg, (*e*) 1 mg.

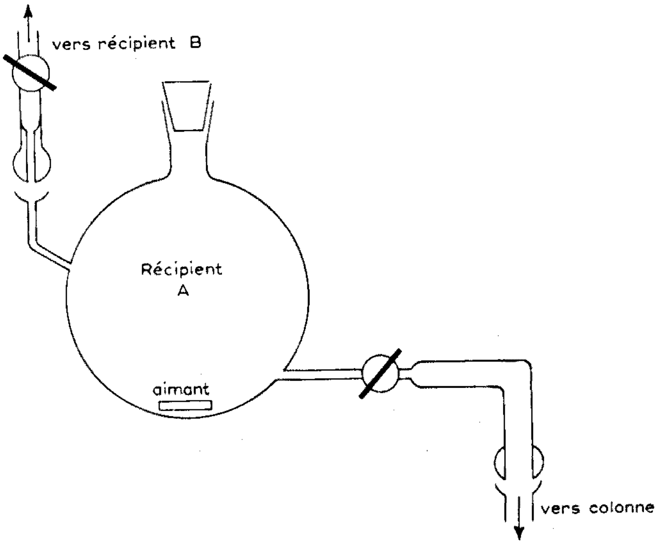

Fig. 3. Appareil à gradient de pH.

Plusieurs auteurs ont appliqué cette technique à la séparation des terres rares, notamment Cornish[6], Nervik[7], Preobrazhensky *et al.*[8], Freiling et Bunney[9], Seyb et Herrmann[4], Clanet[10], Mosen *et al.*[11], Gebauhr et Martin[12]. Wolfsberg[13] a séparé des quantités de 5 mg de diverses terres rares avec l'α-IHBA 0.5 *M* avec gradient d'élution. Cet auteur n'a pas examiné l'influence de la quantité des terres rares sur la constante de distribution. Cette influence ne doit pourtant pas être négligeable, **Deelstra**[5] ayant constaté une grande augmentation du K_D par l'α-IHBA 0.3 *M* avec des quantités d'entraineur d'un mg. Dans le cas présent la technique par gradient de pH fut mis en oeuvre à l'aide d'un système de récipients superposés représenté dans la Fig. 3. Le récipient *A* complètement rempli et muni d'un agitateur magnétique contient la solution de pH initial. Ce récipient est connecté d'une part à la colonne et d'autre part au récipient *B* contenant la solution de pH élevé, le débit de *B* vers *A* étant nécessairement le débit de la colonne. Ce mode opératoire offre l'avantage de ne nécessiter aucun réglage supplémentaire. **Lebreton**[14] a démontré que la concentration C_n, après un débit V_n dans le récipient *A*, est donnée par:

$$C_n = C_p + e^{-V_n/V}(C_0 - C_p) \qquad (1)$$

où
C_n = concentration dans le récipient *A* après passage d'un volume V_n
C_0 = concentration initiale du récipient *A*
C_p = concentration dans le récipient *B*
V_n = volume du récipient *A*.

La variation de pH sera par conséquent donnée par:

$$\text{pH} = \text{p}K_A + \log\frac{C_B}{C_A} = \text{p}K_A + \log\frac{C_p + (C_0 - C_p)\,e^{-V_n/V}}{C_A - [C_p + (C_0 - C_p)\,e^{-V_n/V}]} \qquad (2)$$

où
pK_A = constante d'acidité de l'α-IHBA
C_A = concentration de l'α-IHBA.

La vérification expérimentale de l'équation (2) est représentée dans la Fig. 4.

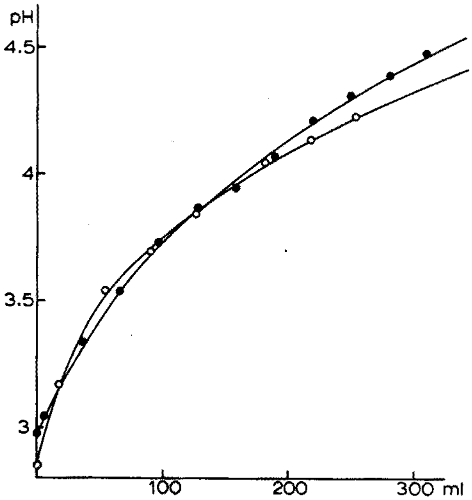

Fig. 4. Gradient de pH: ●—● expérimental, ○—○ calculé.

Les résultats d'une séparation de 1 mg de chaque terre rare à l'aide d'un gradient de pH variant de 3.80–4.05 et de 3.79 à 4.24 sont représentés dans le Tableau I.

Le gradient de pH permet donc de réaliser un gain de temps de respectivement 40% et 50%.

TABLEAU I

CONTAMINATION EN FONCTION DU GRADIENT

Terre rare	*pH 3.83*		*pH 3.80–4.05*		*pH 3.79–4.24*	
	F_{max}	*% Contam.*	F_{max}	*% Contam.*	F_{max}	*% Contam.*
Lu	45.5	0.9	36.9	2.5	32.8	7.5
Yb	65.4	0.0	47.5	0.0	41.2	0.1
Tm	105		65.5		54.1	

La contamination Lu–Yb reste acceptable dans le cas du gradient 3.80–4.05 tandis qu'elle est assez élevée pour un gradient 3.79–4.24. Dans les deux cas la contamination Yb–Tm est négligeable (Fig. 1).

RÉSUMÉ

La séparation Lu–Yb–Tm par l'acide α-hydroxy-isobutyrique 0.1 *M* sur échangeur de cations fut étudiée. La mise en oeuvre d'une quantité de 1 mg de terres rares cause un déplacement considérable de la valeur des constantes de distribution et une asymétrie marquée des pics d'élution. Une séparation quantitative reste cependant possible sans faire appel à une température élevée. La durée de la séparation qui est de l'ordre de 23 h à pH = 3.83 peut être ramenée à 13 h par l'emploi d'un gradient de pH.

SUMMARY

The mutual separation of Lu, Yb and Tm is examined with cation-exchange resin and 0.1 *M* α-hydroxybutyric acid as eluant. When carrier amounts of *ca.* 1 mg of rare earths are eluted, the distribution constants are displaced and the elution peaks are asymmetrical. Quantitative separation is, however, possible at room temperature; separation requires 23 h at pH 3.83 but only 13 h with a pH gradient.

ZUSAMMENFASSUNG

Die Trennung von Lu–Yb–Tm mit einem Kationenaustauscherharz und 0.1 *M* α-Hydroxy-isobuttersäure als Eluierungsmittel wurde untersucht. Wenn Trägersubstanzen der seltenen Erden in Mengen von etwa 1 mg eluiert werden, beobachtet man eine Verschiebung der Verteilungskonstanten und asymmetrische Elutionskurven. Eine Trennung ist jedoch auch bei Zimmertemperatur möglich. Sie benötigt 23 Stunden bei pH 3.83, aber nur 13 Stunden bei einem pH-Gefälle.

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SPECTROPHOTOMETRIC DETERMINATION OF BROMATE WITH *o*-ARSANILIC ACID

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Many color reactions have been proposed for the detection of trace amounts of bromate; examples are strychnine[1], methyl orange[2], indigo carmine[3], oxalic acid–fluorescein[4], oxalic acid–leucofluorescein[5], *p,p'*-dihydroxytriphenylurethane[6], manganous sulfate–benzidine[7] and 3-aminophenoxazine-2-one[8]. All these tests are qualitative.

During a systematic study of the reactivity of twenty-nine selected organic compounds with some seventy-five inorganic ions (in acid, neutral and alkaline media) on a spot plate, it was observed that *o*-arsanilic acid develops a reddish-brown color with bromate ions. This paper presents the study and development of *o*-arsanilic acid as a reagent for the spectrophotometric determination of trace concentrations of bromate.

EXPERIMENTAL

Apparatus

Beckman spectrophotometers, Model DK-2 and Model DU, with 1.000-cm Corex cells, were used.

A Beckman pH meter, Model G, was employed for all pH measurements. It was checked daily with Fisher Certified Standard Buffers.

Reagents

Standard bromate solution. A solution containing 1 mg of bromate per ml was prepared by dissolving 1.306 g of analytical grade potassium bromate in distilled water and diluting to 1 l.

o-*Arsanilic acid solution.* The reagent solution was prepared by dissolving 1.7 g of recrystallized *o*-arsanilic acid (K and K Laboratories, Inc., Jamaica, New York) in 50 ml of distilled water.

All other reagents were analytical grade and were used without further purification.

Procedure

Four solutions are required: (*1*) sample solution free of interfering ions and containing 1 to 500 p.p.m. bromate, (*2*) standard bromate solution, 250 p.p.m., (*3*) nitric acid solution (1 : 10), (*4*) *o*-arsanilic acid solution (1.7 g per 50 ml).

Pour 25 ml of the nitric acid solution into a 50-ml volumetric flask. Pipet a 5-ml aliquot of the sample solution into the volumetric flask. Then pipet a 5-ml aliquot of the reagent solution into the flask, noting the time (use a stop watch) at the beginning of the addition. Dilute immediately to volume with the nitric acid solution and mix thoroughly. The acid normality of the final solution will fall within the range of maximum absorbance. Begin absorbance measurements 5 min after reagent addition. Measure the absorbance at 463 mμ every 60 sec until the absorbance maximum is reached. The maximum exists for about 2 min. Carry out the same procedure using a 5-ml aliquot of the 250 p.p.m. standard bromate solution. A simple calculation then gives the value of the bromate concentration in the sample solution:

$$250 \left(\frac{A_{\text{sample}}}{A_{\text{standard}}}\right) = \text{p.p.m. bromate.}$$

DISCUSSION

Properties of the reagent

o-Arsanilic acid is a white crystalline solid which is soluble in water forming a solution having no absorbance above 400 mμ.

The solution is unstable and decomposes on standing in contact with air. Solutions were prepared daily to avoid interference from reagent decomposition.

Properties of the reaction

Color. Upon adding an *o*-arsanilic acid solution to an acidic bromate solution a reddish-brown color develops at once. The absorbance of the reaction product is dependent upon acidity, time, temperature, presence of redox ions, reagent concentration and bromate concentration but these factors are conveniently controlled in the procedure.

The absorbance of a 40 p.p.m. bromate solution is shown in Fig. 1. The absorbance of the reagent solution could not be distinguished from a distilled water blank above 400 mμ. Maximum absorbance of the reaction product is at 463 mμ.

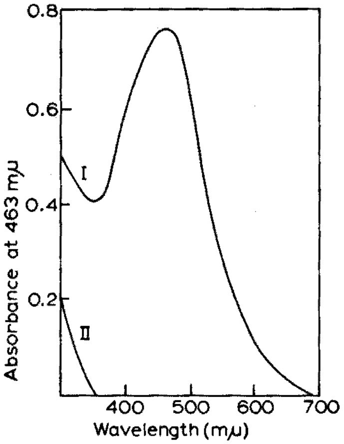

Fig. 1. Absorbance curves for a 40 p.p.m. bromate solution plus reagent (Curve I) and reagent alone (Curve II).

Effect of acidity. The absorbance is affected by the hydrogen ion concentration as shown in Fig. 2. Maximum absorbance occurs at hydrogen ion concentrations of 1.0 to 1.8 *N*. Since this acidity is outside the pH range, a standard method of controlling the acid normality is required.

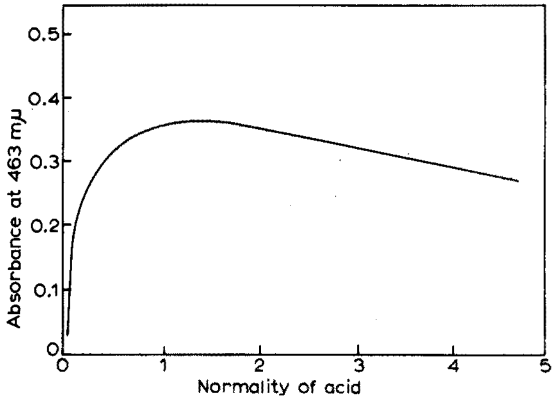

Fig. 2. Effect of acid concentration upon the reaction.

Mole ratio studies. The continuous variation[9,10], mole ratio[11] and slope ratio[12] methods failed to show the existence of a coordination complex. In the absence of a coordination complex, it seems plausible that the color results from a redox reaction.

Effect of temperature. Temperature has a pronounced effect upon the color reaction over the range 15–35°. The reaction rate increases with temperature; the value of the absorbance maximum decreases with temperature. The data for a bromate concentration of 20 p.p.m. are summarized in Table I. The procedure minimizes the temperature effect.

TABLE I

SUMMARY OF TEMPERATURE EFFECTS

Temperature (°)	*Absorbance maximum ($\lambda = 463$ mμ)*	*Time to A_{max} (min)*
15	0.430	24–32
25	0.385	8–9
35	0.340	3

Rate of reaction. Under the conditions of the procedure, maximum absorbance occurs in 8 to 12 min after addition of the reagent. The maximum persists for approximately 2 min and then slowly decreases. Some color, however, remains for at least two weeks. The effect of time on the color reaction is shown in Fig. 3.

Beer's law. The reaction obeys Beer's law up to 50 p.p.m. bromate. This value corresponds to an absorbance of 0.95, approximately the upper limit of the general usefulness of spectrophotometric measurements.

Sensitivity. The limit of identification of the bromate reaction on the spot plate is

0.5 μg of bromate. The dilution limit is 1 : 100,000. To obtain an absorbance of 0.005, a bromate concentration of 0.5 p.p.m. is required. For log $I_0/I = 0.001$, the sensitivity is 0.05 μg BrO_3^- per cm^2.

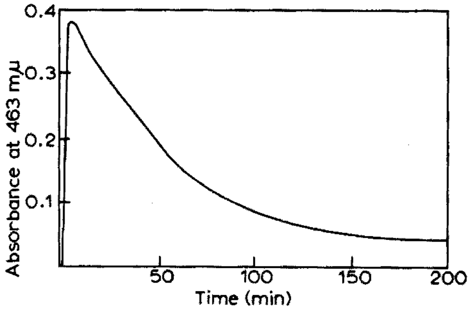

Fig. 3. Effect of time upon the reaction.

Effect of diverse ions. The effect of twenty-one foreign ions was investigated. Interfering ions are arbitrarily defined as those that cause an absorbance change of ±0.005. One hundred parts per million of the following ions give no interference at the 20 p.p.m. bromate level: BO_3^{3-}, CO_3^{2-}, $C_2H_3O_2^-$, $C_2O_4^{2-}$, Cl^-, ClO_3^-, $Cr_2O_7^{2-}$, F^-, PO_4^{3-}, SO_4^{2-}, Co^{2+}, Ce^{3+}, Ni^{2+} and Zn^{2+}. One p.p.m. of the following seven ions interferes to the extent indicated at the 20 p.p.m. bromate level: Br^- (−4%), I^- (+26%), IO_3^- (+3%), NO_2^- (+11%), Au^{3+} (+5%), Ce^{4+} (+11%), Fe^{3+} (+10%).

The reaction of gold(III) with *o*-arsanilic acid has been used as a colorimetric method for the determination of gold[13]. The gold(III) reaction obeys Beer's law but is critically dependent upon temperature, time and acid concentration, indicating a redox reaction.

Precision and accuracy

The precision of the color development was obtained by determining the same amount of bromate (387 p.p.m.) eleven times. The mean value was 387 p.p.m. and the relative standard deviation was 0.95%. In the determination of bromate in various salt solutions (Table II) the standard deviation is 0.52%.

TABLE II

DETERMINATION OF BROMATE IN VARIOUS SALT SOLUTIONS

Solution	*Bromate added (p.p.m.)*	*Bromate found (p.p.m.)*
0.1 *M* $NaC_2H_3O_2$	200	191, 192, 191
0.1 *M* $NaNO_3$	200	191, 191, 192
0.1 *M* Na_2HPO_4	200	191, 194, 192

The procedure was applied to several salt solutions containing 200 p.p.m. in bromate; the results are given in Table II. Various amounts of bromate were also determined in mixed salt solution; the results are summarized in Table III. The mixed salt solutions were 0.1 *M* with respect to sodium acetate, nitrate, and monohydrogen phosphate. A trend in relative error is seen in Table III. Also, it is observed that the closer the bromate concentration in the sample solution is to that in the standard solution, the better the accuracy.

TABLE III

DETERMINATION OF VARYING AMOUNTS OF BROMATE IN MIXED SALT SOLUTIONS

Bromate added (p.p.m.)	*Bromate found (p.p.m.)*	*Relative error (%)*
5	5.9, 5.9	+20
50	55.3, 55.3	+11
100	105, 104	+ 5
200	201, 200	0
500	485, 475	− 4

SUMMARY

o-Arsanilic acid reacts with bromate ions in dilute acid solution and forms a reddish-brown color which is suitable for the spectrophotometric determination of bromate. The reaction has a sensitivity of 0.05 μg BrO_3^- per cm^2 for log $I_0/I = 0.001$ and obeys Beer's law up to 50 p.p.m. The standard deviation for the color development (387 p.p.m. bromate) is 0.95%, and 0.52% in the determination of bromate in salt solutions.

Optimum analytical conditions for the reaction have been established and a procedure for the spectrophotometric determination of bromate is given.

RÉSUMÉ

L'acide *o*-arsanilique réagit avec le bromate, en solution acide, en donnant une coloration brun rougeâtre, permettant un dosage spectrophotométrique de cet anion.

ZUSAMMENFASSUNG

o-Arsanilsäure bildet mit Bromat ein rötlichbraun gefärbtes Reaktionsprodukt, das sich zur spektrophotometrischen Bestimmung von Bromat eignet.

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SPECTROPHOTOMETRIC DETERMINATION OF RARE EARTH METALS WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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The growing importance of rare earth metals in nuclear chemistry and metallurgy has necessitated the development of methods for their rapid determination on the microgram scale. Recently, arsenazo[1], xylenol orange[2], pyrocatechol violet[3], and bromopyrogallol red[4] have been reported as suitable reagents. In these methods many heavy metals and alkali earths interfere. In the present paper the fundamental conditions for the spectrophotometric determination of rare earth metals with 1-(2-pyridylazo)-2-naphthol (PAN)[5] are described.

EXPERIMENTAL

Apparatus and reagents

All measurements were made with a Model EPV-2 Hitachi spectrophotometer with 1-cm cells. A Horiba M-3 type pH meter was used.

Standard solution of rare earth metals. This solution was prepared by dissolving 0.200 g of the pure oxide (99.99% Johnson Matthey) in small amounts of concentrated hydrochloric acid and diluting to 200 ml with distilled water.

1-(2-Pyridylazo)-2-naphthol (PAN) solution. A 0.1% solution was prepared by dissolving 100 mg of PAN (Tokyo Kasei Chem. Co.) in pure methanol.

Buffer solutions. Ammonium chloride–ammonia and sodium acetate–acetic acid solutions were used for the pH adjustment.

Organic solvents were purified by the usual methods. All other reagents used were prepared from analytical grade chemicals or from purified materials.

Procedure

Transfer an aliquot of the slightly acidic solution containing up to 10 μg of rare earth metals to a separatory funnel, and dilute to approximately 20 ml. Add 1 ml of 0.1% PAN solution and 5 ml of buffer solution and allow to stand for several minutes. Add exactly 10.0 ml of ether to the mixture and shake vigorously for 1 to 2 min. Centrifuge the extract and measure the absorbance at 530 or 560 mμ against a reagent blank.

RESULTS AND DISCUSSION

Solvent for extraction

Table I records the colour reactions of the metal–PAN complexes in various common solvents. Ether was the more efficient solvent for the rare earth complexes except in the case of lanthanum, cerium and scandium. The results indicate that ether extraction can be successfully applied to the separation of yttrium from lanthanum, cerium and scandium[5]. The results obtained with carbon tetrachloride and chloroform indicate the possibility of a more extensive application of this sensitive reagent for the mutual separation of rare earth metals.

Absorption spectra

The absorption spectra of the chelates formed with rare earth metals are presented in Fig. 1. Lanthanum, cerium and scandium chelates can not be extracted by ether,

TABLE I

COLOUR REACTIONS OF METAL–PAN COMPLEXES IN VARIOUS SOLVENTS

Solvent	*H_2O*	*CCl_4*	*$CHCl_3$*	*C_6H_6*	*$(C_2H_5)_2O$*
PAN	Yellow	Yellow	Yellow	Yellow	Yellow
La^{3+}	Red ppt.	Orange-yellow	Orange-yellow	Orange-yellow	Orange-yellow
Ce^{3+}	Red ppt.	Orange	Orange	Orange	Orange
Pr^{3+}	Red ppt.	Yellow	Yellow	Yellow	Red
Nd^{3+}	Red ppt.	Yellow	Yellow	Red	Red
Sm^{3+}	Red ppt.	Yellow	Pale red	Red	Red
Eu^{3+}	Red ppt.	Orange-red	Pale red	Red	Red
Gd^{3+}	Red ppt.	Orange-red	Red-orange	Red	Red
Tb^{3+}	Red ppt.	Red	Red-orange	Red	Red
Dy^{3+}	Red ppt.	Red	Red	Red	Red
Ho^{3+}	Red ppt.	Red	Red	Red	Red
Er^{3+}	Red ppt.	Orange-red	Orange-red	Red	Red
Tm^{3+}	Red ppt.	Orange-red	Orange-red	Red	Red
Yb^{3+}	Red ppt.	Orange-red	Orange-red	Red	Red
Lu^{3+}	Red ppt.	Orange-red	Orange-red	Red	Red
Sc^{3+}	Red ppt.	Yellow	Yellow	Yellow	Yellow
Y^{3+}	Red ppt.	Yellow	Yellow	Yellow	Red

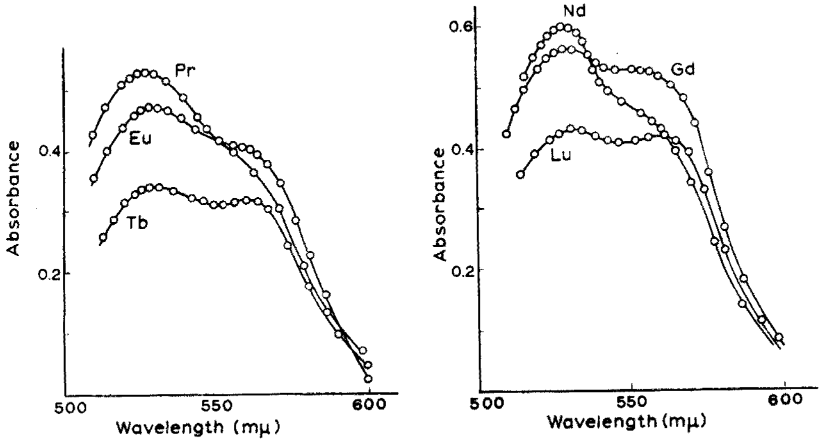

Fig. 1. Absorption spectra of rare earth metal–PAN chelates in ether.

but the other rare earth chelates can be easily extracted by the organic solvent. The absorption maxima of the red chelates in the ether extract appear at approximately 530 and 560 mμ.

Effect of pH

A series of solutions containing definite amounts of rare earth metals and 1 ml of 0.1% PAN solution was prepared. Ammonium chloride–ammonia was used for the pH adjustment. Fig. 2 shows that the optimum pH range was 9 to 10 for praseodymium, samarium, neodymium and gadolinium, and 8 to 10 for dysprosium, europium, and terbium; the optimum pH range for holmium was 8 to 9.5. Below pH 7 no significant complexes were formed between the rare earths and PAN. Similar results were obtained for other rare earth metals.

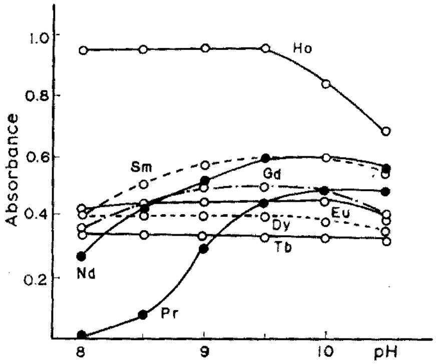

Fig. 2. Effect of pH on absorbance.

Effect of dye

The absorption at pH 10 of a series of solutions, each containing about 10 μg of rare earth metals with varying amounts of reagents, was measured to establish the optimum concentration of the reagent. The results indicated that 1 ml of 0.1% solution sufficed to complex 10 μg of metal ion.

Time of standing and stability of colour

The minimum time for standing before extraction with ether for complete colour development of the rare earth metal–PAN chelates was 10 min. After this time, the colour of the ether extract was usually very stable and suitable for quantitative work. For example, the samarium and gadolinium complexes were stable for at least 2 h; the neodymium complex was stable for 1 h but the praseodymium complex was much less stable.

Beer's law and sensitivity

The absorbances of the ether extracts of the rare earth metal–PAN chelates were found to be linearly related to the concentration of rare earth metals, and conformed to Beer's law up to approximately 2 μg per ml. The molar extinction coefficients of each of the rare earth chelates calculated from Beer's law are listed in Table II.

TABLE II

MOLAR EXTINCTION COEFFICIENTS

Metals	*Molar extinction coefficient ε*	*Wavelength (mμ)*
Nd	80,000	530
Sm	78,000	530
Eu	62,000	530
Gd	66,000	530
Tb	68,500	530
Dy	65,000	530
Ho	68,000	530
Er	64,000	530
Tm	65,000	530
Yb	57,000	530
Lu	70,000	530
Y	66,000	530

Composition of the complex

The empirical formula of the coloured complexes of the rare earth metals was determined by adopting the continuous variation and mole ratio methods. Within experimental error the results suggest that 1 : 2 complexes of the rare earth metals with the reagent were formed.

Back extraction

Rare earth metals in the combined organic phase could be back-extracted by an acidic solution.

Interferences

The effects of nearly all the elements associated with rare earth metals were studied to determine their behaviour with PAN under the optimum conditions used above.

Citric acid and potassium cyanide did not interfere. The rare earth metals could be determined in the presence of many foreign metals. Aluminium (1 mg), beryllium (0.5 mg), chromium (0.1 mg), molybdenum (0.05 mg), nickel (0.1 mg), zinc (0.1 mg), magnesium (0.5 mg), calcium (0.1 mg), tin (0.2 mg), thorium (0.2 mg), vanadate (0.2 mg), and fluoride (0.1 mg) did not interfere.

The amount of uranium which could be present was limited; 100 μg could be tolerated if a preliminary extraction was done at pH 6; at this pH the complex between rare earths and PAN was not formed. Small amounts of iron be could removed by back-extraction or a colorimetric determination could be done simultaneously.

SUMMARY

1-(2-Pyridylazo)-2-naphthol (PAN) reacts very sensitively with rare earth metals to form a deep red precipitate in alkaline solution; this can be extracted with ether, except in the case of lanthanum, cerium and scandium. Absorption maxima occur at 530 and 560 mμ. Traces of rare earth metals may be determined in the presence of many foreign metals.

RÉSUMÉ

Le 1-(2-pyridylazo)-2-naphtol (PAN) réagit, avec une grande sensibilité, avec les métaux des terres rares, pour donner un précipité rouge, en solution alcaline. Une extraction à l'éther est possible, sauf dans le cas du lanthane, du cérium et du scandium. Des traces de terres rares peuvent ainsi être dosées en présence de plusieurs métaux étrangers.

ZUSAMMENFASSUNG

1-(2-Pyridyl-azo)-2-naphtol (PAN) bildet mit den Metallen der seltenen Erden in alkalischem Medium tiefrot gefärbte Niederschlage. Diese können mit Aether extrahiert werden mit Ausnahme von Lanthan, Cer und Scandium. Die Absorptionsmaxima liegen bei 530 und 560 mμ. Nach dieser Methode können Spuren von Metallen der seltenen Erden neben vielen Fremdmetallen bestimmt werden.

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Short Communications

Atomic absorption spectroscopy of aluminum

A literature survey reveals that atomic absorption spectroscopy utilizing the flame atomization technique has not been successful when applied to the determination of certain elements.[1-5] Among these elements are aluminum, silicon, zirconium, cadmium, niobium, tantalum, etc. The reason for this failure appears to be the formation of refractive compounds in the flame, thus leaving virtually no free atoms, so that there is no atomic absorption. Robinson[2-4] reported that he could not obtain any atomic absorption of aluminum by any flame, not even by an oxy-cyanogen flame (4550°C). In his latest paper[2], he confirmed the above observation and demonstrated that aluminum in the ground state can be obtained by using an electric spark in place of a flame. This was demonstrated with the aid of an electric discharge for the atomization and an ARL Quantometer for measurement. The present authors have succeeded in determining aluminum by atomic absorption spectroscopy using either oxy-acetylene or oxy-hydrogen flames boosted by an organic aerosol containing an aluminum complex.

Experimental

Apparatus. The atomic absorption spectrophotometer used in these studies has been designed and built by Kem-Tech Laboratories, Inc. It has a prism monochromator covering a range 200–700 mμ and a frequency selective photomultiplier detection unit coupled with a recorder read-out system. An aluminum hollow cathode lamp (Ransley Glass Instruments, Melbourne, Australia) modulated at 60 c.p.s. was used as a radiation source.

Reagents. Aluminum standard solutions were prepared by dissolving chemically pure aluminum metal in conc. hydrochloric acid. The solution was diluted to a known volume with demineralized water. A Beckman integral type of aspirator-burner was used for sample atomization. All chemicals used were of reagent grade.

Procedure. Aluminum was extracted into an organic solvent as follows. An aqueous solution of aluminum was buffered with ammonium acetate and its pH adjusted to 3.5. A freshly prepared aqueous solution of ammonium salt of N-nitrosophenylhydroxylamine (cupferron) was added, and the aluminum cupferrate chelate was extracted into 4-methyl-2-pentanone. The organic phase was aspirated into both oxy-acetylene and oxy-hydrogen flames. The absorption was measured at 396.2–394.4 mμ using a spectral slit-width of 6.2 mμ. The optimum experimental conditions found were: oxygen: 10 psi; acetylene: 7.5 psi; flow rate, oxygen: 4.0 l/min, acetylene: 2.2 l/min; oxygen/fuel ratio: 1.8. Each point on the calibration curves was established by calculating the mean of 10–12 consecutive timed readings. These readings were closely bracketed with readings of reagent blanks.

Results and discussion

Preliminary observations indicated a low level of aluminum absorption. Calibration curves were therefore prepared with aluminum concentrations ranging from 50–2500 p.p.m. A calibration curve with an oxy-acetylene flame was nearly linear over the range 50–1500 p.p.m.; absorption readings above 1500 p.p.m. were too erratic for accurate measurement. The calibration curve with an oxy-hydrogen flame was nearly linear over the 500–2500 p.p.m. The regions below and above these limits were not investigated.

The use of an oxy-acetylene flame increases the sensitivity about nine-fold over that of oxy-hydrogen. A 100 p.p.m. aluminum solution with an aspiration rate of 3.8 ml/min produced a 6.4 mV signal when oxy-acetylene was used. Actual experiments using an oxy-acetylene flame established a 36 p.p.m. detection limit.

The most critical experimental parameter controlling sensitivity was found to be the flame position through which radiation passed from the hollow cathode lamp. A displacement of 1 cm in vertical height or a somewhat smaller lateral displacement was found to make the difference between detection and no detection. This perhaps explains why previous workers failed to detect aluminum absorption in flames.

A highly reducing flame is calculated to be the most favorable medium to inhibit oxide formation. However, in the flame used, free oxygen atoms and molecules are present. This oxygen induces the formation of AlO ($\mathrm{Al}^\circ + \mathrm{O} \rightarrow \mathrm{AlO}$). A very high temperature is required to dissociate AlO to produce an adequate population of ground state aluminum in the flame. The higher the temperature of the flame, the greater the dissociation of AlO. Only an oxy-fuel flame containing an organic aerosol possesses sufficient energy for the dissociation of $\mathrm{AlO} \rightarrow \mathrm{Al}^\circ + \mathrm{O}$. The estimated temperature[6] with oxy-acetylene flame fed with 4-methyl-2-pentanone aerosol is in the range of 3450°K. Although with this elevated temperature, the molecular dissociation of AlO increases, the large value[7–8] (138 kcal) of dissociation energy demands that the bulk of aluminum still exists as AlO. This may account for the rather low sensitivity of aluminum. Observations made during this study indicate the possibility that organic solvents and complexes aid in detection by means other than temperature enhancement of the flame (this was also considered possible by Robinson[9–10]). Further, it is possible that the point of detection is in the transition between the complex breakdown and the formation of AlO. Further work is necessary to elucidate the mechanism of dissociation more clearly. The experimental evidence that the sensitivity is low and that the flame position is extremely critical points to the fact that the life of ground state aluminum (before oxidation to AlO) is extremely short.

Higher sensitivity (3 p.p.m. or better)[2] can be achieved by using a much higher temperature such as a spark. Such an increase in sensitivity would be achieved only at the sacrifice of simplicity of technique, ease of manipulation, and low cost of instrumentation, thus detracting seriously from the merits of flame absorption spectroscopy. Further work is in progress, and details will be shortly published.

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The spectrophotometric determination of some organic acids with copper benzidine

A simple and rapid procedure for determining microgram quantities of various organic acids and their salts is often very useful in chemical studies of aqueous solutions after radiation treatment. In these cases, acidimetric titrations are not suitable and are inapplicable for salt solutions. The presence of hydrogen peroxide limits the use of titrations with potassium permanganate, and also often renders difficult the use of colorimetric methods. In our laboratory, in many cases, the method previously developed for oxalic acid[1] has been used; this involves a spectrophotometric determination with copper–benzidine.

The mechanism of this reaction is not quite clear although some salts of copper–benzidine, such as sulphates and acetates[2], have long been known. In the case of concentrated solutions of oxalic acid, it is assumed[3] that the acid reacts with the reagent (a 5% solution of benzidine in 5% acetic acid and 0.2 *N* copper acetate) to produce a compound of the following form: $[Cu^{2+}(C_{12}H_8(NH_2)_2)_n]C_2O_4$.

Preliminary measurements showed that in spectrophotometric determinations, the molar ratio of copper acetate to benzidine should be larger than one, which is the opposite of what would be expected; from the results obtained the optimum ratio is three. Benzidine itself has a very strong absorbance in the working region and its maximum concentration in the measured solution has to be limited to $1.25 \cdot 10^{-3}$ *M*.

Reagents

Solution A. Prepare a $1.25 \cdot 10^{-3}$ *M* benzidine hydrochloride solution by carefully dissolving a measured quantity of the substance in 30% acetic acid and then diluting with distilled water. The amount of acetic acid depends on the total amount of solution A; 1 ml is added for each 100 ml of the solution.

Solution B is $3.75 \cdot 10^{-3}$ *M* copper acetate, obtained by a direct dissolution of the substance in water.

For the reagent solution, equal volumes of solutions A and B.

Procedure

Measure an appropriate amount of the test solution into a 25-ml volumetric flask. Add 5 ml of the reagent solution and then dilute with water to the mark. Use 5 ml of the reagent solution diluted to 25 ml with water in the reference cell. If the solutions are prepared in smaller or larger flasks, proportional amounts of the reagent must be taken. Transfer the solutions to 1-cm cells and measure the absorbance. Experimental data for the measurements are given in Tables I and II.

Results and discussion

The reaction with copper–benzidine is instantaneous at room temperature. The solutions A and B, as well as the mixed reagent are stable under normal laboratory conditions for at least 10 days. The absorbance of the prepared sample solutions remains unchanged for 24 h.

The temperature coefficients were measured at temperatures between 18 and 30° and the data are given in the last column in Tables I and II; as can be seen, the tem-

TABLE I

EXPERIMENTAL DATA FOR ACIDS

Acid	*Working wavelength (mμ)*	*Molar absorbance at 24°*	*Validity region of Lambert–Beer's law (M)*	*Temperature coefficient for 1° (%)*
Oxalic	246	2.490	$1.4 \cdot 10^{-5}$– $4 \cdot 10^{-4}$	—0.7
Tartaric	243	1.255	$3 \cdot 10^{-5}$–$3.5 \cdot 10^{-4}$	—0.7
Malonic	242	2.380	$1.5 \cdot 10^{-5}$–$2.0 \cdot 10^{-4}$	—0.4
Citric	242	2.184	$2 \cdot 10^{-5}$–$1.3 \cdot 10^{-4}$	—0.25
Lactic	242	398	$9 \cdot 10^{-5}$– $5 \cdot 10^{-4}$	—0.7
Glycolic	243	367	$1.5 \cdot 10^{-4}$– $8 \cdot 10^{-4}$	—0.4
Formic	244	249	$1.5 \cdot 10^{-4}$–$1.2 \cdot 10^{-3}$	—0.8
Succinic	244	151	$2.4 \cdot 10^{-4}$–$1.6 \cdot 10^{-3}$	—0.8

TABLE II

EXPERIMENTAL DATA FOR SALTS

Compound	*Working wavelength ($m\mu$)*	*Molar absorbance at 24°*	*Validity region of Lambert–Beer's law (M)*	*Temperature coefficient for 1° (%)*
Potassium oxalate	254	1.530	$2.5 \cdot 10^{-5}$–$4.5 \cdot 10^{-5}$	—0.2
Potassium sodium tartrate	233	692	$5 \cdot 10^{-5}$– $5 \cdot 10^{-4}$	—0.25
Sodium formate	284	177	$2 \cdot 10^{-4}$– $8 \cdot 10^{-4}$	—0.9

perature absorbance coefficients are considerable and all measurements should be made at constant temperatures. It is important to equalize the temperatures of the sample and reference solutions before the optical densities are read; otherwise, the measured absorbances do not become constant for some time, because the temperature coefficient of the reagent with the substance is different from that of the reference solution. For instance, with water as the reference solution, the temperature coefficient of the reagent with oxalic acid is −0.5% per 1°, whereas that of the reagent alone with pure water is +0.8% per 1°.

Special attention should also be paid to the purity of the benzidine hydrochloride. The molar absorbance depends greatly on the purity of benzidine and may vary up to 10% even without any visible change in the absorption spectra. Benzidine was purified by recrystallization from hot aqueous solution with the addition of concentrated hydrochloric acid to the cold solution: the benzidine hydrochloride obtained is more stable and suitable for work than benzidine itself. An occasional check of the molar absorbance is a good check of the purity of benzidine.

The procedure described allows direct, individual spectrophotometric determination of the following organic acids and some of their salts: oxalic, tartaric ,malonic, citric, lactic, glycolic, formic and succinic acids.

The absorption spectra of the acids and some salts are shown in Figs. 1 and 2 and further data are given in Tables I and II. It can be seen that the absorption spectra of salts are different from those of the parent acids; they are broader and their maxima are shifted, the molar absorbances being smaller. This is certainly due to the presence of cations and the change in pH. It was also found that the molar absorbance decreases with increase in pH; for example, when the pH of potassium oxalate is increased from 7 to 12, there is a 10% decrease in the molar absorbance.

As can be seen from Figs. 1 and 2, simultaneous determinations are not usually possible because the absorption spectra are similar and their absorption maxima very close. Tables I and II, however, show that the difference in molar absorbances makes it possible in some cases to determine, with somewhat lower accuracy, some of the acids in the presence of others (for example, large amounts of oxalic acid in the presence of small concentrations of formic or succinic acids, etc.).

Oxalic, malonic, tartaric and citric acids, as well as the oxalates and tartrates, can be quite easily determined with an accuracy of ± 2% because of the somewhat larger validity region of Lambert–Beer's law and the higher molar absorbance. Determinations of lactic, glycolic, formic and succinic acids, as well as the formates, are less accurate (± 5%). In the latter case, better results could probably be obtained by varying the concentrations of benzidine and copper acetate, as well as their proportions. It should be mentioned also that the procedure described should be suitable for the determination of organic acids other than those mentioned.

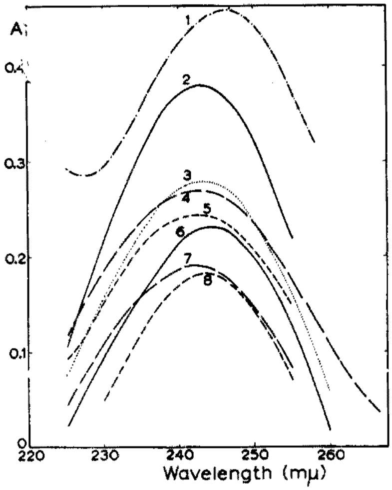

Fig. 1. Absorption spectra for acids.
1 Oxalic ($1.9 \cdot 10^{-4}$ M);
2 Tartaric ($3.2 \cdot 10^{-4}$ M);
3 Glycolic ($7.5 \cdot 10^{-4}$ M);
4 Malonic ($1.18 \cdot 10^{-4}$ M);
5 Citric ($1.25 \cdot 10^{-4}$ M);
6 Succinic ($1.6 \cdot 10^{-3}$ M);
7 Lactic ($4.7 \cdot 10^{-4}$ M);
8 Formic ($7.25 \cdot 10^{-4}$ M).

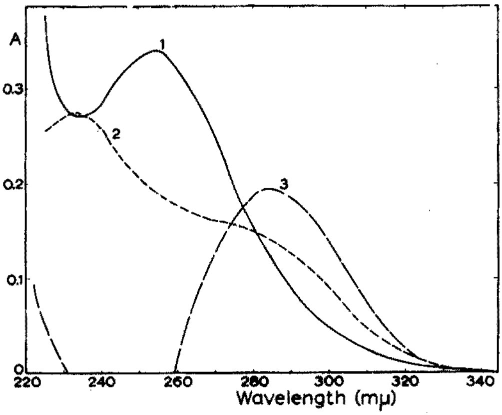

Fig. 2. Absorption spectra for some salts.
1 Potassium oxalate ($4 \cdot 10^{-4}$ M);
2 Potassium sodium tartrate ($4 \cdot 10^{-4}$ M);
3 Sodium formate ($1.1 \cdot 10^{-3}$ M).

The method is sensitive, direct, simple and fast. The presence of hydrogen peroxide in concentrations smaller than 0.01 M does not affect the accuracy of the results, which is important in radiation experiments. Complete details will be published elsewhere[4].

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Analytical applications of the reaction of hexacyanoferrate(III) with ascorbic acid

Part VI. Determination of hydrazine[1]

The simple, rapid and accurate titrimetric determination of hexacyanoferrate(III) with ascorbic acid[2] and the favourable redox potential of the hexacyanoferrate (III)–(II) system can be utilised for the determination of several oxidising or reducing ions[1,3].

The reaction between hydrazine and hexacyanoferrate(III) in alkaline medium yields nitrogen gas and hexacyanoferrate(II) ions[4].

$$N_2H_4 + 4(Fe(CN)_6)^{3-} + 4\,OH^- \longrightarrow N_2 + 4\,(Fe(CN)_6)^{4-} + 4\,H_2O$$

Determinations of hydrazine have been described involving measurement of the nitrogen evolved[4] or cerimetric titration of the hexacyanoferrate(II) formed[5]. Potentiometric titrations of hexacyanoferrate(III) with standard hydrazine sulphate solution[6] and the simultaneous determination of hydrazine and hydroxylamine have also been reported. The present method is based on the oxidation of hydrazine in a moderately alkaline solution with hexacyanoferrate(III), excess of which is titrated with ascorbic acid. The reaction is rather slow, therefore the solution must be left to stand for about 30 min before titration.

Reagents

The preparations of 0.1 *N* ascorbic acid solution, 0.1 *N* potassium hexacyanoferrate-(III) solution, boric acid–borax buffer and 2,6-dichlorophenolindophenol indicator solution have already been described[1,3].

Hydrazine sulphate solution. $N_2H_4 \cdot H_2SO_4$ was used to prepare a 0.1 *N* (0.025 *M*) solution. The solution was standardized iodometrically by addition of an excess of iodine, making alkaline with sodium hydroxide, acidification after 2 min, and titration with ascorbic acid.

Procedure

Two titrations are needed; the first serves to standardize the ascorbic acid, and the second is the determination itself.

(*1*) To 30.00 ml of 0.1 *N* potassium hexacyanoferrate(III) solution, add 1–2 g of solid potassium hydrogen carbonate and 1 ml of the indicator (or 0.5 g of the solid mixture). Titrate the green solution with 0.1 *N* ascorbic acid to colourless (*A* ml).

(*2*) To 30.00 ml of 0.1 *N* potassium hexacyanoferrate(III) solution, add 40 ml of the buffer solution and then add the unknown sample containing 4–15 mg of hydrazine. Mix the solution and leave for 30 min. Acidify slightly with 1:1 (v/v) hydrochloric acid, and add 1–2 g of potassium hydrogen carbonate. Add the indicator as above and titrate with 0.1 *N* ascorbic acid to colourless. If *B* ml is consumed, the volume of 0.1 *N* ascorbic acid (V) equivalent to the hydrazine present is calculated from the equation: $V = (A - B)\,f$, where f is the factor for the titrant.

Results of some hydrazine determinations are shown in Table I. The standard deviation calculated from 12 parallel results is ±0.22%, while the standard deviation of the mean is ±0.07%.

TABLE I

ASCORBINOMETRIC DETERMINATION OF HYDRAZINE

Hydrazine taken (mg)	*Hydrazine found (mg)*	*Error %*	
		Maximum	*Minimum*
3.88	3.86 (3 results)	−0.72	±0.00
7.75	7.76 (12 results)	+0.36	±0.00
11.63	11.65 (3 results)	+0.03	±0.00
15.49	15.49 (3 results)	+0.13	+0.07

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Book Reviews

Analyse der Metalle, II. Band, *Betriebsanalysen*, in zwei Teilen. Zweite neu bearbeitete Auflage, I. Teil, *Aluminium bis Schwefel*, XVI/1–726, II. Teil, *Selen bis Zirkonium und physikal.-chem. Verfahren*, IV/727–1586 und 227 Abbildungen, Springer Verlag, Berlin-Göttingen-Heidelberg, für Chemikerausschuss der Gesellschaft Deutscher Metallhütten- und Bergleute e.V., 1961, DM 158,—.

Die Notwendigkeit der Schaffung einer neu bearbeiteten zweiten Auflage des erst vor sechs Jahren erschienenen Werkes „Betriebsanalyse" zeigt allein schon, dass es sich hier um ein sehr geschätztes, viel gebrauchtes und oft gesuchtes Arbeits- und Nachschlagewerk handelt. Der in zwei Teilen vorliegende zweite Band „Analyse der Metalle" behandelt in 45 Kapiteln zuerst in alphabetischer Reihenfolge die Elemente Aluminium bis Zirkonium und beinhaltet alle für die Beurteilung von Ausgangs-, Zwischen- und Endprodukten notwendigen Betriebsmethoden. Anschliessend werden in acht weiteren Kapiteln auch die in der Metallindustrie häufig vorkommenden Fragen der Brennstoff-, Gas- und Wasseruntersuchung abgehandelt. Auch die Kapitel über die theoretischen und apparativen Grundlagen moderner physikalisch-chemischer Verfahren sind sehr gut abgefasst und entsprechen dem modernsten Stand der

Betriebsanalysentechnik, sind sie doch von den hervorragendsten Fachleuten verfasst worden. Wertvoll sind auch die Kapitel über Lösungen, z.B. Pufferlösungen und besonders auch jene über die genormten Metalle und Legierungen.

Die Gliederung der einzelnen Elemente in Unterkapitel ist ausgezeichnet und gibt jedem Leser sofort einen Überblick über Vorkommen und qualitative Nachweismöglichkeiten des betreffenden Elementes, um dann volle Auskunft über die quantitative Bestimmung dieses Elementes in Ausgangsprodukte (Erze etc.) und Anreicherungs-, Zwischen- und Endprodukte zu geben. Jede Methode wiederum ist unterteilt in:

(1) Grundlage, wobei sowohl chemische als auch gewisse arbeitstechnische Besonderheiten berührt werden.

(2) Anwendungsbereich und Bedeutung. Gerade dieses Unterkapitel ist immer wichtig und bewahrt oft von vornherein vor einer Fehlanwendung der entsprechenden Methode.

(3) Weist auch fast jede Methode eine Genauigkeitsstufe, die zwischen 1 und 3 variieren kann, auf.

Unter Genauigkeitsstufe 1 werden jene Verfahren verstanden, die entweder selbst als Schiedsanalyse üblich sind, oder in ihrer Genauigkeit den Anforderungen an eine Schiedsanalyse gerecht werden; die Genauigkeitsstufe 2 gibt an, dass dieses Verfahren die für übliche Betriebsanforderungen notwendige Genauigkeit zumindest erreicht, während Genauigkeitsstufe 3 erkennen lässt, dass mit dieser Methode nur Annäherungswerte erreichbar sind. Es wird meist der zur Analysendurchführung notwendige Zeitbedarf (auch ein wichtiger Faktor in der heutigen Zeit) angegeben, sowie besondere Hinweise auf Lösungen, Störungen und Literaturstellen. Der Referent möchte an dieser Stelle einen kleinen Vorschlag für die kommende Neuauflage machen und dies wäre die Einfügung eines kleinen Kapitels über Statistik einschliesslich Fehlerrechnung usw.

Dieses Werk ist in seiner Gesamtheit nicht nur ein wichtiges Standardwerk für jedes Betriebslaboratorium, sondern auch ein unentbehrliches Buch für die Ausbildung und zum Nachschlagen. Ein besonderer Vorteil liegt auch noch darin, dass es sowohl für vorzüglich bis gut als auch für einfach ausgerüstete Laboratorien gleich gut geeignet ist und daher auch nirgends fehlen darf.

H. MALISSA (Wien)

Anal. Chim. Acta, 28 (1963) 399–400

Spectroscopy, edited by M. J. WELLS, Institute of Petroleum and Pergamon Press, London, 1962, viii+305 pp., 63s.

This interesting volume cannot justifiably claim to be "a balanced appreciation of spectroscopy as it stands today". It is a collection of twenty-one contributions, of from three to thirty pages in length, presented at a London Conference in March 1962. The emphasis is on spectra in relation to molecular structure. In addition to aspects of i.r., u.v., n.m.r. and e.s.r. spectra there are stimulating essays on flash photolysis and flame spectra of free radicals. At least half of the contributions provide excellent brief accounts of their topics; perhaps Ingram on e.s.r. and Wilkinson on far i.r. spectra can be given special mention. The item on "The use of computers in spectroscopy" — featured in the Pergamon Press blurb — amounts to two and a half

Anal. Chim. Acta, 28 (1963) 400–401

pages; even though these are by A. D. Booth, they can only mention some of the features involved.

Industrial scientists or Honours B.Sc. students seeking brief accounts of current developments will find good material in this volume.

MANSEL DAVIES (Aberystwyth)

Anal. Chim. Acta, 28 (1963) 400–401

Mises au Point de Chimie Analytique Pure et Appliqué, publiées sous la Direction de J. A. GAUTIER, Professeur à la Faculté de Pharmacie de Paris, 10ème série, Masson et Cie, Paris, 1962, 258 pages, 55 NF.

Comme les ouvrages précédents, celui-ci rassemble les exposés faits au cours de l'année sur des sujets variés à la Faculté de Pharmacie de Paris:

(1) *Applications des osmopiles galvaniques à la détection et au dosage des produits toxiques-volatils* par A. BERTON. L'auteur décrit des titrages ampérométriques, au moyen de deux électrodes de natures différentes, de substances toxiques volatiles. Il décèle ainsi 1 p.p.m. de gaz sulfureux dans l'air et aussi de nombreux corps organiques dans des mélanges.

(2) *L'hydrure de lithium-aluminium comme réactif en analyse organique* par E. A. M. DAHMEN. Excellente revue sur les propriétés de ce composé et ses applications analytiques (105 références).

(3) *La fermentation alcoolique en fonction du milieu* par L. GENEVOIS. (90 références).

(4) *Quelques aspects de la chromatographie en phase vapeur en biochimie* par J. BARAUD. Etude des produits volatils de la fermentation.

(5) *Humidité et extrait sec des matières alimentaires et des médicaments* par J. KIGER. Mise au point très importante (108 pages) concernant les propriétés générales de l'eau dans les matières alimentaires, la précision des déterminations et les causes d'erreur, une revue des méthodes de dosage et la description très détaillée des principales méthodes utilisées, avec figures.

Dans une seconde partie l'auteur traite de l'eau dans les produits pharmaceutiques et des dosages selon la pharmacopée française (pour 200 corps), selon la pharmacopée internationale et selon la pharmacopée américaine.

(6) *Constantes d'ionisation et structures des composés organiques* par P. RUMPF. Définitions des acides et des bases et détermination des constantes; structure et acidité.

Le choix des sujets, et des auteurs, dû au Professeur Gautier fait de cette 10ème série, comme des précédentes, un ouvrage qui intéressera tous les analystes.

G. CHARLOT (Paris)

Anal. Chim. Acta, 28 (1963) 401

Treatise on Analytical Chemistry, édité par I. M. KOLTHOFF et P. J. ELVING avec la collaboration de E. B. SANDELL, Part II, *Analytical Chemistry of the Elements*, Vol. 9, Interscience–Wiley, New York, 1962, 135 s.

Ce volume est consacré à l'étude de l'uranium et des éléments transuraniens y compris le lawrencium. Ces éléments sont présentés par quatre spécialistes: G. L. Boomann, C. F. Metz, J. E. Rein et G. R. Waterbury.

188 pages sont consacrées à l'uranium et la partie la plus spectaculaire est évidemment celle qui traite des transuraniens dont nous citerons, à titre d'exemple, et pour montrer combien ce livre est riche en substances, les chapitres les plus importants de la première partie qui traitent du neptunium, du plutonium et de l'américium:

Synthèses, propriétés physiques, chimiques, optiques et électrochimiques.

Dissolution et séparation: électrodéposition, extraction par solvant, systèmes chélates, échangeurs anions-cations, volatilisation. Détection et identification: couleur des ions, spectres d'émission et d'absorption, spectres de fluorescence X, propriétés radiochimiques.

Détermination des éléments: méthodes radiochimiques, spectrophotométriques, polarographiques, méthodes à potentiel contrôlé, gravimétrie, volumétrie, rayons X, méthodes spectrographiques, spectrographie de masse.

Analyses des impuretés, détermination des gaz, des non-métaux, des métaux, détermination des impuretés par spectrographie, détermination des produits de fission et des autres produits radioactifs par les méthodes radiochimiques, etc . . .

On peut se rendre compte qu'on y trouve une foule de documents et de renseignements en partie inédits dans ce domaine très nouveau. La bibliographie va jusqu'en 1960 et la présentation, comme pour tous les autres volumes, est parfaite.

D. MONNIER (Genève)

Anal. Chim. Acta, 28 (1963) 401–402

Neutronenaktivierung als analytische Hilfsmittel, von WERNER SCHULZE unter Mitwirkung von WERNER BOCK-WERTHMANN, *(Die Chemische Analyse*, herausgegeben von G. JANDER), Ferdinand Enke Verlag, Stuttgart, 1962, 323 pp., Geheftet, DM 75; Ganzleinen, DM 79.

In Dr Schulze's book a most valuable survey is given of the rapidly expanding field of activation analysis. After outlining the principles and advantages of this technique the author gives a short survey of neutron sources. A more detailed description of modern neutron generators would perhaps be welcome here. He then deals successively with the qualitative and quantitative aspects of neutron irradiations and secondary reactors, from a theoretical and practical viewpoint. Separate chapters deal with the different decay modes of radioactive species, the measuring techniques, the identification of isotopes and chemical procedures. The author finally discusses in the last descriptive chapter special activation procedures for some light (H, He, Li, Be, B, C, N, O) and heavy (Th, U) elements. The second part of the book is devoted to a very well made survey of the literature with over 1000 references.

The third part consists of the following tables:

(1) nuclides with cross sections, (2) decay properties of radionuclides, (3) gamma emitters listed with increasing energy, (4) radionuclides listed with increasing half-lives, (5) interfering reactions for each element, (6) activities obtained after different irradiation periods for each element, together with the fractions due to β, γ and electron capture decay, (7) detection limits for β-counting in a given geometry, (8) simplified schemes of gamma spectra.

Anal. Chim. Acta, 28 (1963) 402–403

This book will certainly be of excellent value to chemists interested in the possibilities of activation analysis and for the more experienced worker already familiar with this technique.

J. HOSTE (Gent)

Anal. Chim. Acta, 28 (1963) 402–403

Methods of Organic Elemental Microanalysis, by G. INGRAM, Chapman & Hall, London, 1962, XVI + 511 pp., 75s.

In den letzten Jahren sind mehrere Bücher erschienen, die das gleiche Thema behandeln, aber — und dies soll gleich einleitend betont werden — das zur Besprechung vorliegende Werk ist eines der besten! Der Autor hat sich ausschliesslich auf elementaranalytische Methoden beschränkt, diese aber dafür ausführlich und gründlich an Hand von über 100 Abbildungen beschrieben. Die klassischen Methoden — und heute zählen ja alle PREGL'schen Verfahren zu diesen — sind zwar erwähnt, aber nicht mehr im Einzelnen beschrieben. Dies ist vor allem für solche Leser wichtig, die an Hand dieses Buches darangehen wollen, ein Mikrolaboratorium einzurichten. Nachteilig ist für diesen Leserkreis vielleicht die Tatsache, dass keinerlei Informationen über Mikrowaagen und die Wägetechnik enthalten sind, sodass ein Anfänger sich die entsprechenden Angaben aus anderen Werken entnehmen muss.

Das Buch besteht aus drei Teilen und einem Anhang. Im ersten Teil werden verschiedenen Methoden zur Bestimmung von Kohlenstoff, Wasserstoff, Sauerstoff, Stickstoff, Halogenen und Schwefel behandelt. Der schnellen Verbrennung im leeren Rohr, die ja vom Autor mitentwickelt wurde, ist entsprechend viel Raum gegeben worden, ohne dass aber dadurch andere Verfahren benachteiligt wurden. Vorteilhaft ist ferner, dass bei den Kapiteln Halogen- und Schwefelbestimmung zahlreiche Methoden zur Endbestimmung angegeben werden. Für die Schwefelbestimmung ist die Bariumperchloratmethode im Vergleich zu ihrer Bedeutung etwas zu kurz behandelt, während die gravimetrische Bestimmung, die heute fast nicht mehr verwendet wird, in extenso beschrieben wird.

Im zweiten Teil werden Methoden zur Bestimmung von insgesamt 37 Metallen und Nichtmetallen soweit sie in organischen Verbindungen vorkommen können, beschrieben. Dieser Teil ist äusserst wertvoll, da, soweit dem Referenten bekannt, in keiner der bisher erschienenen Monographien über organische Mikroelementaranalyse, solche zusammengefasst und derart ausführlich beschrieben sind. Auch in diesem Abschnitt sind meist mehrere Endbestimmungsmethoden angeführt. Zu bedauern ist lediglich, dass die elegante Methode zur massanalytischen Bestimmung des Phosphors von PÜSCHEL und WITTMANN nicht aufgenommen wurde.

Im dritten Teil werden einige Methoden zur Mikrogrammanalyse — d.h. Verfahren für eine Einwaagegrösse von *ca.* 50 μg — angegeben. Diese Methoden haben gerade in den letzten Jahren immer mehr Bedeutung erlangt, und es ist begrüssenswert, dass nunmehr ein Buch vorliegt, in dem die verschiedenen in der Fachliteratur angegeben Verfahren gesammelt und ausführlich beschrieben worden sind. Nach einem einleitenden Kapitel wird die OERTLING-Mikrogrammwaage kurz beschrieben und ebenfalls kurz auf das Umgehen mit kleinsten Flüssigkeitsmengen eingegangen. Von den verschiedenen bekannten "Ultramikrobüretten" ist nur die Agla-Bürette erwähnt.

Anal. Chim. Acta, 28 (1963) 403–404

Die Feststellung, dass andere Büretten für Mengen unter 1 ml nicht die gleiche Präzision haben, wie die im Buch erwähnte, kann allerdings nicht unwidersprochen bleiben. In den folgenden Kapiteln dieses Abschnittes werden Methoden zur Bestimmung der am häufigsten vorkommenden Elemente (C,H, N, Halogene, S und P) angeführt.

Schliesslich wird im Anhang zunächst auf die Probenahme, Trocknungsmethoden, Reinigung der Probe (etwas kurz) und Bestimmung des Wassergehaltes eingegangen. Während die Schmelzpunkts- und Molekulargewichtsbestimmung nur erwähnt sind, ist die Siedepunktbestimmung nach EMICH etwas ausführlicher beschrieben. Ferner wird die Herstellung von Urtiter- und Masslösungen beschrieben. Schliesslich sind noch in einer Tabelle die Testverbindungen zusammengefasst, welche von einem Komittee der Microchemistry Group der Society for Analytical Chemistry empfohlen wurden. Hier wäre es wünchenswert gewesen, die von der IUPAC-Kommission für Mikrochemischen Methoden empfohlenen Substanzen zu kennzeichnen.

Zusammenfassend lässt sich sagen, dass das Buch bestens empfohlen werden kann. Es bietet nicht nur dem angehenden Analytiker, sondern auch dem schon mehr oder minder lange auf diesem Gebiet tätigen, eine Menge wertvoller Informationen, sodass es eigentlich in keinem mikroanalytischen Laboratorium fehlen dürfte.

W. SCHÖNIGER (Basel)

Anal. Chim. Acta, 28 (1963) 403–404

Announcement

SYMPOSIUM ON THIN-LAYER CHROMATOGRAPHY

An International Symposium on Thin-Layer Chromatography will be held at the Istituto Superiore di Sanità, Rome, Italy, on May 2nd and 3rd, 1963. The lecturers will include Prof. Stahl, Ing. Labler, Dr. Demole, Dr. Wollenweber, Prof. Marini-Bettòlo, and Dr. M. Lederer. One afternoon will be devoted to original papers.

Participants desiring to present a paper should submit a short summary to the organiser not later than **April 15th.**

Applications and enquiries should be addressed to Prof. G.B. Marini-Bettòlo, Istituto Superiore di Sanità, Viale Regina Elena 299, Rome, Italy.

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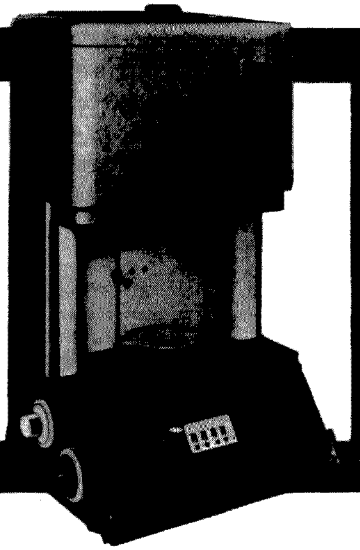

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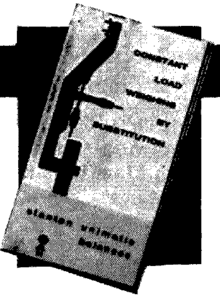

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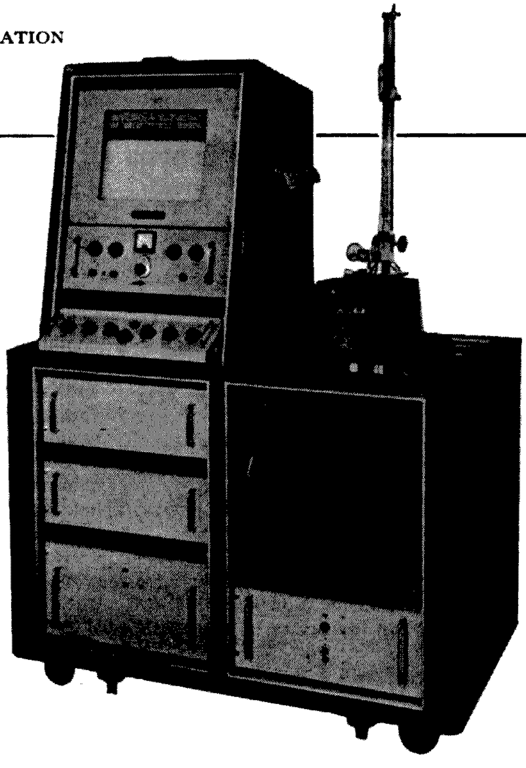

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