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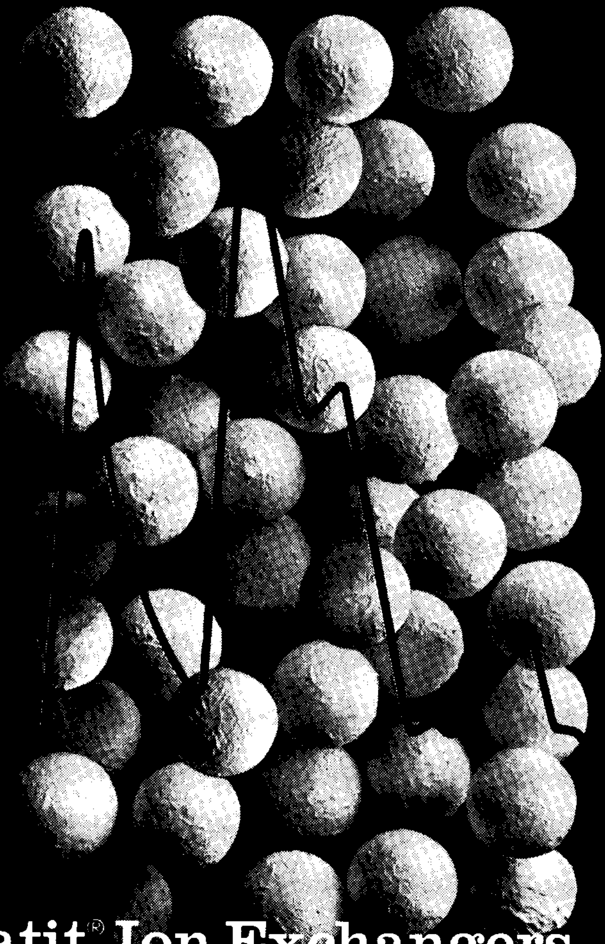

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ION-SELECTIVE ELECTRODES BASED ON SILVER SULPHIDE

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(Received 6th May 1972)

The study of the electrochemical properties of the sulphides of heavy metals has a long tradition. Since the beginning of the century sporadic studies have been made of the sulphides of silver, copper, lead, iron and several other metals[1-8]. In these experiments, however, sulphides of different composition and even minerals were used, and some of the conclusions reached are therefore not in full agreement with each other.

About five years ago the renaissance of potentiometry led to the introduction of the reversible silver sulphide electrode, and several analytical studies with this electrode have already been published[9-15]. The silver sulphide electrodes used in these recent studies are probably dissimilar only with respect to the composition of the membranes, regardless of whether they are pressed tablets[16], single crystals or mixtures of silver sulphide and an inert matrix such as silicone rubber[11], polyethylene[14] or others. The electrode characteristics are determined by the chemical properties of the silver sulphide used and they should therefore be practically the same for different types of membranes if the same silver sulphide precipitate is used.

This study is dedicated to a comparison of electrodes whose silver sulphide membranes have been prepared in different ways, and the effect on sensitivity and selectivity is illustrated. The response to cyanide and mercury(II) ions, the effect of exposure to light, and the standard potential of the electrodes, are also discussed.

EXPERIMENTAL

Apparatus

The silver sulphide electrodes used in this study were a Sulphide Electrode, Crytur model 16–17 (Czechoslovakia) and several silver sulphide electrodes of laboratory preparation with membranes of pressed tablets. The reference electrodes were saturated calomel electrodes, Radiometer type K701, with a double salt-bridge filled with either 0.1 M sodium nitrate or saturated potassium nitrate.

A digital pH meter, type PHM52, was used for potential measurements in connection with a Servograph Recorder, type REC51. For pH measurements a pH meter, type PHM25 SE, was used in conjunction with a combination pH electrode, type GK2301C; for measurements of redox potential a silver metal electrode, type P401, was used. All the above types of equipment are manufactured by Radiometer A/S, Copenhagen (Denmark).

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All measurements were carried out in thermostatted vessels at 25° with either a water thermostat, type VTS13 (Radiometer A/S) or an Ultra-Thermostat U-10 (VEB, Dresden, DDR).

Reagents

Chemicals of analytical grade (Merck and BDH) were used without further purification. Stock solutions of sodium sulphide and sodium cyanide were freshly prepared every second day and protected by an inert atmosphere. During measurements in sulphide solutions, nitrogen of special purity ("Extra Dry", Chr. Nielsen A/S, Strandmøllen, Denmark) was bubbled through the solutions. Stock solutions of silver nitrate were protected against light, and measurements in solutions containing silver ions were carried out in polyethylene vessels.

Generally, all solutions were balanced to ionic strength $\mu = 0.1$ with sodium nitrate. In the few cases where a different ionic strength was used, this is mentioned specially.

Preparation of electrodes

Silver sulphide may be precipitated from solutions containing an excess of either silver or sulphur, and one of the aims of this study was to demonstrate the effect thereof on the electrode characteristics.

The electrodes A and B were prepared from a batch of silver sulphide precipitated from a solution containing a 3% excess of sulphur. The material used for electrode A was further purified by extraction with carbon disulphide and should therefore be closer to stoichiometric composition than the material used for electrode B. Electrode C was made from silver sulphide precipitated from a solution containing a 3% excess of silver. Electrodes of type D were prepared from silver sulphide which was precipitated from a solution containing a 0–3 % excess of either silver or sulphide, and which was carefully purified by washing with complexing agent, nitric acid and carbon disulphide.

RESULTS

Overall sensitivity

The potential of the Crytur electrode as a function of pAg or pS is shown in Fig. 1. Similar characteristics were found for the electrodes A, B, C and D.

Measurements at a_{Ag^+} of $7.5 \cdot 10^{-2}$ (0.1 M $AgNO_3$) and $1.5 \cdot 10^{-23}$ (0.01 M sulphide at pH = 11.8) were used to estimate the overall sensitivity of the electrodes. The corresponding potential differences for the electrodes A, B, C and D were 1283 ± 1.5 mV against 1276 mV for the Crytur electrode.

In the range from pAg 6 to pAg 20 in Fig. 1, measurements in solutions of the sodium salts of chloride, bromide and iodide were used to demonstrate the linear relationship between the electrode potential and pAg instead of measurements in diluted solutions of silver nitrate and sodium sulphide. To stabilize the silver activity in the above halide solutions, it was necessary to add a small amount of the corresponding silver halide. Otherwise the electrode potentials would be too negative, as can be seen from Fig. 1 at the points 6, 9 and 11.

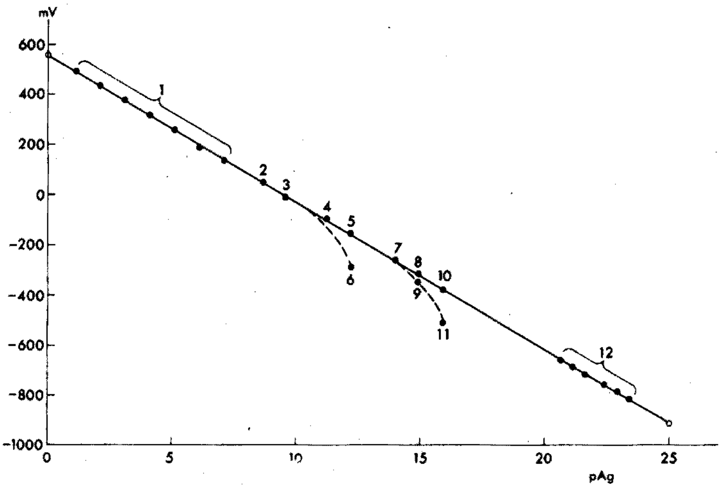


Fig. 1. Overall sensitivity of the silver sulphide electrodes. (1) solutions of $AgNO_3$ ($\mu = 0.1$), 10^{-1} to 10^{-7} *M*; (2) 0.1 *M* NaCl; (3) 1 *M* NaCl, sat. with AgCl; (4) 0.1 *M* NaBr; (5) 1 *M* NaBr, sat. with AgBr; (6) 1 *M* NaBr, unsaturated; (7) 0.01 *M* NaI; (8) 0.1 *M* NaI, sat. with AgI; (9) 0.1 *M* NaI, unsat.; (10) 1 *M* NaI, sat. with AgI; (11) 1 *M* NaI, unsat.; and (12) 0.01 *M* Na_2S ($\mu = 0.11$), pH 7.0 to pH 12.0.

Standard potentials of silver sulphide electrodes

The standard potentials of the electrodes were found by extrapolating the potentials in silver solutions to the values corresponding to $a_{Ag^+} = 1$, and using 242.0 mV as the potential of the reference S.C.E. at 25°[17]. The observed standard potentials for all 5 types of electrodes had an average value of $E_0 = 800.1 \pm 1.1$ mV, when the existence of junction potentials was left out of account.

Changing the internal contact from an Ag/AgI electrolyte to a direct metal contact as described by Körbl *et al.*[18] caused the standard potential to depart from the above value, as seen in Table I, where experimental values of E_0 for the A electrode are listed for different contacting materials.

This effect was further investigated by using the same silver sulphide precipitate as used for the membrane of electrode A for silver sulphide electrodes with graphite contacts. These electrodes were made by impregnating the electrode body of a graphite-filled polymer, either superficially (I) or thoroughly (II) with the silver sulphide precipitate, by means of a compression technique[19]. The experimental E_0 values of these electrodes are also included in Table I.

TABLE I

E_0 VALUES OBTAINED WITH DIFFERENT INTERNAL CONTACTS

Contact material	Electrolyte	Ag	Cu & Zn	Hg	Pt	Pb & Sn	Graphite + PTFE	
							I(A)[b]	II(D)[b]
E_0(mV)[a]	800	845	910	945	970	990	800–830	1010

[a] Owing to drift up to ~2 mV min, the figures were rounded off to 5 mV.

[b] The letters A and D refer to the precipitates used.

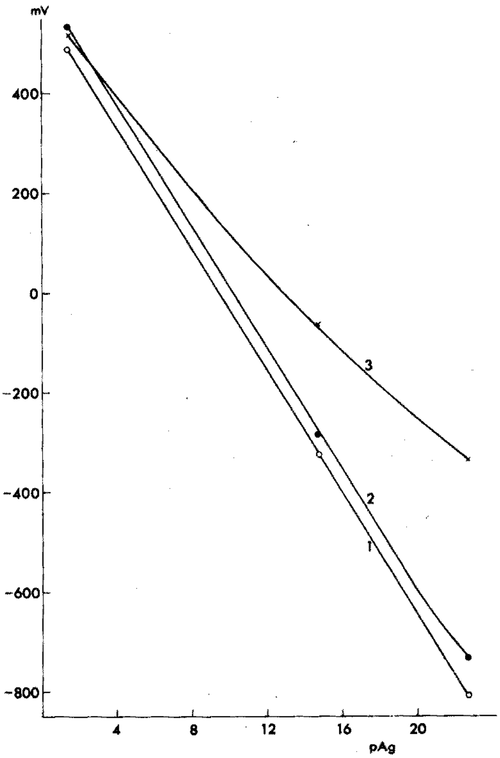


Fig. 2. Influence of the type of inner contact on the potentials of silver sulphide electrodes. (1) 0.1 *M* $AgNO_3$ electrolyte, (2) metallic silver, (3) graphite–PTFE mixture[19].

In addition to deviations from the original standard potential, a loss of sensitivity and bad reproducibility of the potentials were generally observed for the electrodes which had direct metal contact with the silver suphide membrane. Calibration curves of the electrodes with electrolytic (1), silver (2) and graphite (3) contacts are shown in Fig. 2.

Sensitivity to sulphide

The relationship between sulphide activity and electrode potential was tested in a $4.2 \cdot 10^{-3}$ *M* solution of sodium sulphide. Measurements were made in borate buffer solutions in the pH range 9.32–12.32 where the sulphide ion is largely hydrolyzed:

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^- \tag{1}$$

The sulphide activity is defined by pH or a_{H^+} according to:

$$a_{S^{2-}} = \frac{\gamma_{S^{2-}}[S^{2-}]_{tot}}{1 + a_{H^+}/K_2} \tag{2}$$

$\gamma_{S^{2-}} = 0.38$ at $\mu = 0.1$[20], and the value $10^{-12.9}$ is selected as the best estimate for the hydrolysis constant, K_2, according to Ringbom[21].

As the silver sulphide electrodes are sensitive only to the S^{2-} ions and not to

SH^- ions, a potential change of 29.58 mV per unit of pH at 25° should be observed. Experimentally, the following values were obtained:

Electrode A	29.37 mV per unit of pH
Electrode B	29.25 mV per unit of pH
Electrode C	29.81 mV per unit of pH
Electrode D	29.74 mV per unit of pH
Electrode Crytur	33.0 mV per unit of pH

The supersensitivity of the Crytur electrode decreased to 31.5 mV/pH when the electrode was polished before each measurement. A metallic silver electrode gave results varying from 28.7 to 30.5 mV/pH, because of drifting potentials. The practical measuring range for sulphide ions is limited to 10^0–10^{-5} *M* total sulphide content and pH 8–14 when these electrodes are used.

Sensitivity to silver (I)

All of the electrodes showed very reproducible potentials in dilution series of silver nitrate in the range 10^{-1}–10^{-5} *M* silver(I). At lower concentrations, adsorption of silver to the electrode bodies, measuring vessels and reference electrodes will cause a noticeable deviation from the theoretical sensitivity[22]. Adsorption of silver on the membrane surface also diminished the sensitivity and caused hysteresis effects. These phenomena could be overcome by flushing the vessels and electrodes with dilute nitric acid and polishing the membranes when changing from concentrated to diluted silver ion solutions. Provided that these precautions were taken and that the measurements were carried out in polyethylene vessels, the sensitivity of the electrodes was in accordance with a theoretical sensitivity of 59.16 mV for a tenfold change of silver ion activity in the concentration range 10^0–10^{-7} *M* silver(I), although the response time below 10^{-5} *M* amounted to several minutes. Calibration curves under different measuring conditions are shown in Fig. 3.

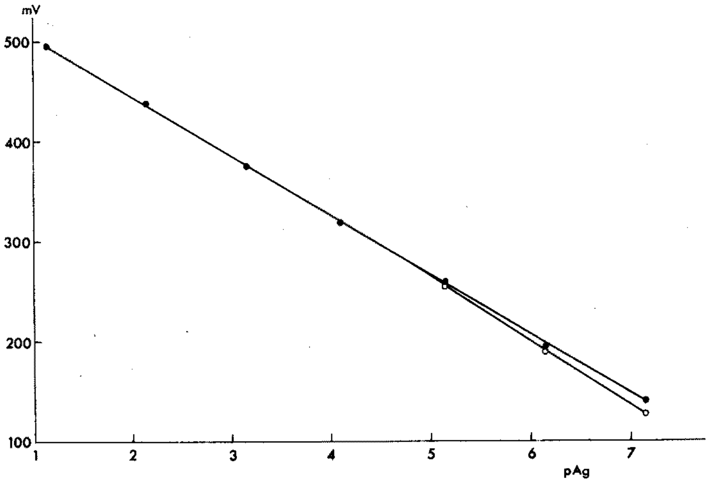


Fig. 3. Silver sensitivity of electrode D. Concentration range 10^{-1}–10^{-7} *M* Ag^+ at $\mu = 0.1$ ($NaNO_3$). (●) Stirred samples; (○) unstirred samples.

Selectivity and interferences

Generally, ions or chemicals that may react with either silver ions or sulphide ions must be regarded as interfering substances. In simple cases, the interference from other ions with the electrode potential can be described by the equation:

$$E = E_0 \pm \frac{RT}{nF} \ln[a_i + K_{ij}(a_j)^{n/m}] \tag{3}$$

where a_i is the activity of the primary ion, *i.e.*, Ag^+ or S^{2-}, a_j the activity of the interfering ions. R, T and F are the conventional constants of the Nernst equation, n is the valence of the primary ion, and m is the valence of the interfering ions. On the assumption that eqn. (3) is valid, the selectivity ratios, K_{ij}, were calculated from the potentials of the electrode in 0.1 M solutions of the primary ions and the interfering ions, respectively, with the activity coefficients of Kielland[20]. These equal 0.755 at $\mu = 0.1$ for the monovalent ions in question (Ag^+, Cl^-, Br^-, I^-, NO_3^- and OH^-); for divalent ions, the values $\gamma_{S^{2-}} = 0.38$ at $\mu = 0.1$, $\gamma_{Cu^{2+}} = 0.29$ and $\gamma_{Pb^{2+}} = 0.20$ at $\mu = 0.3$, were used.

The selectivity ratios found by measurements with electrodes A, B, C, D and with the Crytur electrode, are listed in the Tables II and III. The theoretical values were calculated from the appropriate solubility products[21,23], as it was assumed that the electrodes respond directly only to silver and sulphur ions. The good agreement between theoretical and measured selectivity ratios for chloride, bromide and iodide is the reason for using halide solutions as indirect pAg standard solutions for measuring the overall electrode sensitivity above.

TABLE II

SELECTIVITY RATIOS OF THE SILVER SULPHIDE ELECTRODES AS Ag^+-SENSING ELECTRODES

Ratio	*Theoretical*[a]	*Crytur*	*A*	*B*	*C*	*D*
$K_{Ag^+/Cu^{2+}}$	$9 \cdot 10^{-8}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	$2 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$5 \cdot 10^{-7}$
$K_{Ag^+/Pb^{2+}}$	$9 \cdot 10^{-12}$	$1 \cdot 10^{-6}$	$8 \cdot 10^{-9}$	$2 \cdot 10^{-9}$	$1 \cdot 10^{-8}$	$5 \cdot 10^{-11}$
K_{Ag^+/H^+}	$4 \cdot 10^{-12}$	$9 \cdot 10^{-6}$	$4 \cdot 10^{-7}$	$3 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$6 \cdot 10^{-12}$

TABLE III

SELECTIVITY RATIOS OF THE SILVER SULPHIDE ELECTRODES AS S^{2-}-SENSING ELECTRODES

Ratio	*Theoretical*[a]	*Crytur*	*A*	*B*	*C*	*D*
K_{S^{2-}/Cl^-}	$7 \cdot 10^{-30}$	$3 \cdot 10^{-31}$	—	—	—	$2 \cdot 10^{-31}$
K_{S^{2-}/Br^-}	$2 \cdot 10^{-26}$	$5 \cdot 10^{-26}$	$5 \cdot 10^{-26}$	$5 \cdot 10^{-26}$	$5 \cdot 10^{-26}$	$2 \cdot 10^{-26}$
K_{S^{2-}/I^-}	$8 \cdot 10^{-19}$	$2 \cdot 10^{-18}$	$2 \cdot 10^{-18}$	$2 \cdot 10^{-18}$	$2 \cdot 10^{-18}$	$6 \cdot 10^{-19}$
K_{S^{2-}/OH^-}	$\sim 10^{-35}$	$8 \cdot 10^{-27}$	$2 \cdot 10^{-20}$	$2 \cdot 10^{-18}$	$3 \cdot 10^{-27}$	—

[a] Solubility products given in ref. 23 and $-\log K_{HS^-} = 12.9$ were used.

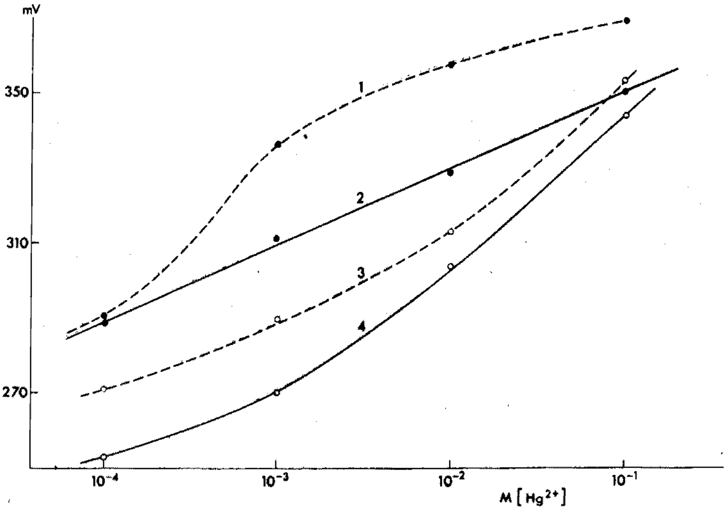


Fig. 4. Sensitivity of silver sulphide electrodes to mercury(II). (●) Newly polished electrode in: (1) unstirred samples and (2) stirred samples. (○) Aged electrode in: (3) unstirred samples and (4) stirred samples. All measurements were made by stepwise decreasing mercury(II) concentrations at $pH = 1.3$, $\mu = 0.6$.

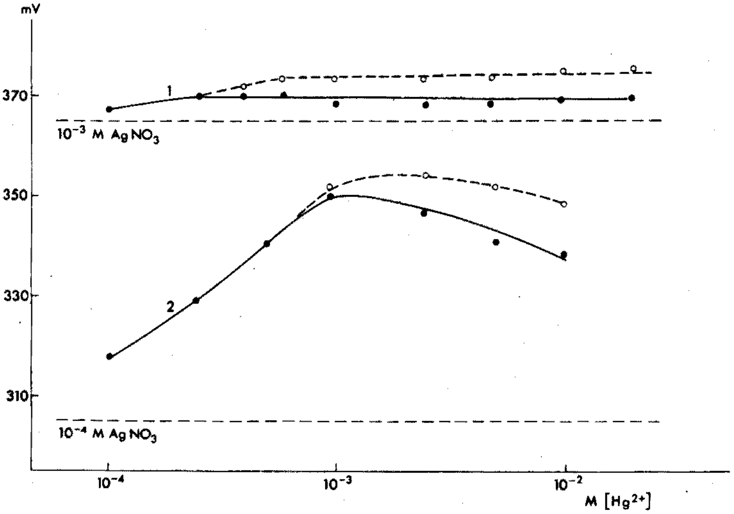
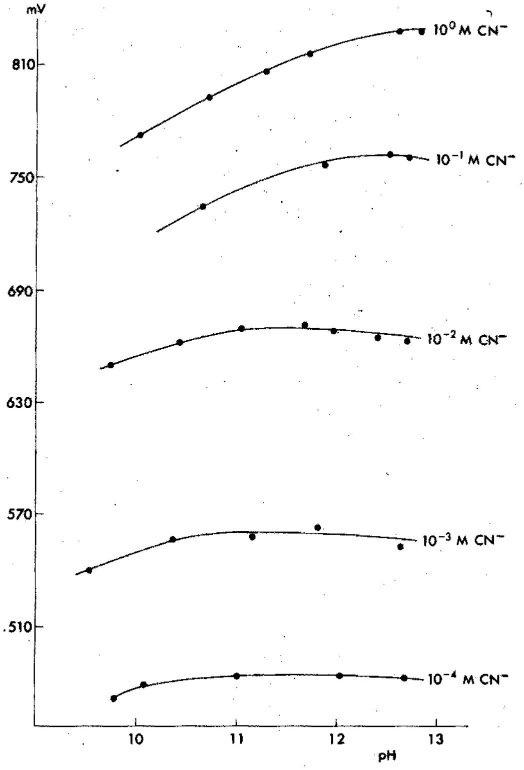


Fig. 5. Interference of mercury(II) with the silver response of silver sulphide electrodes. (1) 10^{-3} M $AgNO_3$, (2) 10^{-4} M $AgNO_3$. (●) Stirred samples and (○) unstirred samples. (-----) Level in the Hg^{2+}-free $AgNO_3$ samples.

Severe interferences occurred when the electrodes were used in solutions of mercury(II) ions which form a still less soluble sulphide than silver sulphide. Figure 4 illustrates the mercury(II) response of the Crytur electrode; Fig. 5 shows how the presence of mercury(II) ions interferes with the silver response at two different silver concentrations. To obtain a reasonable stability in solutions containing mercury(II), the electrode had to be polished before each measurement, but even then the potentials were badly reproducible, drifting and characterized by oscillations amounting to ±2 to ±3 mV. The measured potentials were highly sensitive to stirring as seen in

Fig. 4, and it seems inadequate to describe the mercury(II) response of the electrode in an equation of the type of eqn. (3).

Cyanide can form strong complexes with silver ions (Ag $[CN]_3^{2-}$ with $\beta_3 = 10^{21.98}$ and Ag $[CN]_2^-$ with $\beta_2 = 10^{20.44}$)[24], and cyanide may accordingly interfere with sulphide in controlling the electrode potential. The dependence of the potential of electrode A on pH at total cyanide concentrations ranging from 10^0 to 10^{-4} M is given in Fig. 6. The cyanide response of the silver sulphide electrode cannot be described in a Nernstian electrode equation of type (3). The response of the electrode as a cyanide-sensing electrode compared with that of a metallic silver electrode, both at pH 11, is shown in Fig. 7. The electrodes behave quite differently, but although non-Nernstian, the cyanide response of the silver sulphide electrode is more stable and less dependent on stirring than that of the metal electrode.



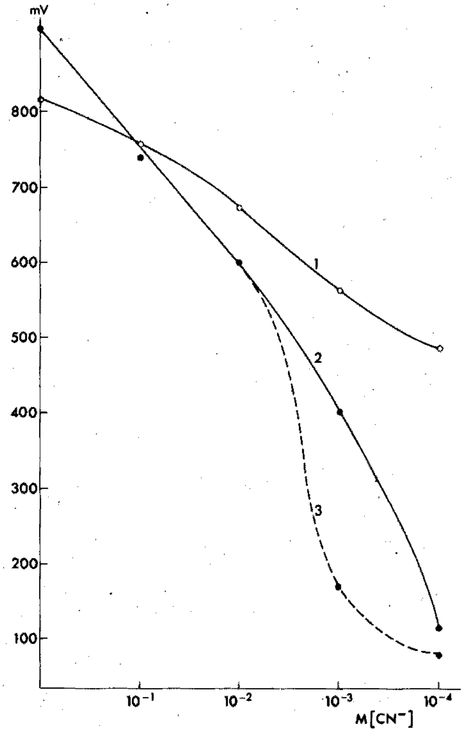


Fig. 6. Cyanide sensitivity of silver sulphide electrodes as a function of pH in hydroxide–borate buffers.

Fig. 7. Cyanide sensitivity of silver sulphide and metallic silver electrodes at pH 11.7. (1) The Ag_2S electrode; (2) metallic silver electrode in stirred samples; (3) metallic silver electrode in unstirred samples.

Sensitivity to light

Illumination with visible light may influence electrode potentials, as is known from silver halide electrodes[25]. This effect was investigated for the Crytur silver sulphide electrode at intensities up to about 400 lux with light from fluorescent tubes.

In solutions of 10^{-1}, 10^{-3}, 10^{-5} M silver nitrate and in 10^{-1} M sodium iodide with solid silver iodide, the light influenced the electrode potential by less than 0.1 mV, but in a sulphide solution ($[S^{2-}] = 3 \cdot 10^{-4}\,M$), a change of $+0.9 \pm 0.2$ mV was observed at 400 lux. However, in all cases, a transient shift of about 2 mV was observed, negative at a shift to high intensity, positive at a shift to low intensity. The stable value of the potential was obtained within 5 s, and the effect was similar to what has been observed before for classical silver halide electrodes[26].

DISCUSSION

From the measurements of the overall sensitivity it is clear that the silver sulphide electrodes all behave as ideal silver electrodes, at least in the pAg range 1–23, when the solubility product of silver sulphide is assumed as a best estimate[21] to be $10^{-49.2}$. As sulphide-sensing electrodes the corresponding range for pS is 3–47, but the analytical application of these electrodes at low concentrations of sulphide or silver(I) may be limited, because of secondary effects such as adsorption of silver ions, oxidation of sulphide or contamination by impurities, if no sulphide- or silver–buffering system is present.

Whereas the sensitivity of the different types of electrodes is almost the same, electrodes with membranes having a stoichiometric composition, A and D, or a small excess of sulphur, B, are superior as regards selectivity, which confirms earlier observations[7,17]. An excess of silver, as in the case of electrode C, gives poorer selectivity ratios for interfering cations, but suppresses the apparent interference of hydroxyl ions. Since the Crytur electrode with a single-crystal membrane has nearly the same selectivity properties as electrode C, its membrane will probably also contain an excess of silver—possibly developed by the crystal-growth process.

Standard potentials

The standard potentials of the electrodes with electrolyte as the inner contact are closer to +799.1 mV, which is the standard potential of the Ag/Ag^+ electrode[23], than to +850 mV, which has been suggested as the standard potential of Ag_2S/Ag^+[27]. With metal and graphite internal contacts, standard potentials in the interval 0.80 V to 1.01 V were obtained. Such a variation of E_0 must be regarded as the result of the charge-transfer mechanisms in the membrane and at the membrane interfaces. A similar effect has previously been observed for silver halide electrodes[28] with different contact metals, but in that case there was no departure of E_0 with a silver contact, *i.e.*, these electrodes behave as ideal second-order halogenide electrodes.

For silver sulphide membranes it has been suggested that the electrochemical properties may be ascribed to an adsorption mechanism[29], to the free mobility of silver ions in silver sulphide[30], or to silver sulphide as an electronic semiconductor with micro-amounts of free silver and sulphur in equilibrium with the bulk Ag_2S, which allows of two electrode reactions:

$$Ag \rightleftharpoons Ag^+ + e \qquad E_0 = +0.7991\text{ V} \tag{4}$$

$$Ag_2S \rightleftharpoons 2Ag^+ + S + 2e \qquad E_0 = +1.008\text{ V} \tag{5}$$

The E_0 value of eqn. (5) was derived from the E_0 value of eqn. (4) and -9.62 kcal mole^{-1} as the standard free energy for silver sulphide[31].

The present experiments give no evidence as to which hypothesis is correct.

A membrane between two silver(I)-containing electrolytes with a Ag/Ag$^+$ inner reference electrode will be symmetric, *i.e.*, the E_0 value of eqn. (4) should be observed regardless of whether the charge transfer in the membrane is ionic or electronic, and of whether the surface reaction is due to adsorption, transfer of free silver ions, or one of the electrode reactions (4) or (5). In the case of metallic contact, a change from electronic to ionic charge transfer will take place at one of the membrane interfaces, and the standard potential will depend on which of the reactions (4) or (5) is responsible for the change from electronic to ionic charge transfer. In the extreme case, eqn. (5) may replace eqn. (4) to describe the overall electrode reaction.

Interferences

Interfering substances usually influence the electrode potential according to selectivity ratios which can be derived theoretically from the appropriate solubility products. As seen from Tables II and III, the theoretical selectivity ratios for halides, and also for such cations as lead and copper, correlate well with the values found in these experiments, especially when some of the precipitates in question were added to the solution.

In the case of strongly interfering species, *e.g.*, mercury(II) or cyanide ions, the problems are more complex, and the measured potentials are not only the result of a chemical equilibrium, but the kinetic conditions at the electrode surface must also be considered.

According to the solubility product of mercury(II) sulphide[21], the selectivity ratio to be used in eqn. (3) to describe the interference of mercury(II) with the silver response of a silver sulphide electrode should be above 20. The measured interferences are significantly smaller, but also poorly reproducible and strongly dependent on the stirring rate. This indicates that a layer of mercury sulphide is deposited on the surface of silver sulphide. This layer forms a diffusion barrier for the exchanging Hg^{2+} and Ag$^+$ ions, which reduces the apparent selectivity ratio, but which also is responsible for the anomalies and instabilities of the response to mercury(II).

Cyanide response

At high concentrations of cyanide the following exchange reaction can occur at the membrane surface:

$$6\,CN^- + Ag_2S \rightleftharpoons S^{2-} + 2\,Ag\,(CN)_3^{2-} \tag{6}$$

This reaction will build up a steady-state sulphide activity at the electrode surface. If it is assumed that the sulphide activity is almost half the Ag (CN)$_3^{2-}$ activity, owing to the reaction stoichiometry, and that the cyanide activity at the electrode surface is only slightly reduced, an apparent $K_{S,CN}$ can be derived. If the differences in diffusion rates of the ions involved are neglected, and the values $\beta_3 = 10^{22.0}$ for the Ag(CN)$_3^{2-}$ complex and $K_{S0} = 10^{-49.2}$ for Ag$_2$S are accepted, the interference in concentrated cyanide solutions should be described by:

$$E = E_0 - 29.6 \cdot \log(a_{S^{2-}} + K_{S,CN} \cdot a^2_{CN^-}) \tag{7}$$

where

$$K_{S,CN} = (0.25 \cdot K_{S0} \cdot \beta_3^2)^{\frac{1}{3}} \cong 10^{-1.9}$$

Actually, $K_{S,CN}$ from the measurements in 1 M potassium cyanide (Fig. 6) can be estimated at about $10^{-2.2}$, which is in good agreement with the theory above. The pH dependence in 0.1 M and 1 M cyanide solutions corresponds to the pK_2 of hydrogen sulphide, which proves the above linking of the cyanide response to the sulphide ion.

Below 10^{-2} M cyanide the potential of the silver sulphide electrode becomes less dependent on pH (for pH > 10), and it changes at a rate exceeding 59.2 mV per tenfold reduction of cyanide activity, which corresponds to the above expression (7) for the sensitivity to cyanide. If a_{CN^-} is below 10^{-2}, the inherent S^{2-} activity according to reaction (6) should be less than 10^{-6}, which is below the practical working range of the silver sulphide electrode as a sulphide-sensing electrode. Below 10^{-2} it could be assumed that the formation of the dicyano–silver complex would take over the potential control according to:

$$4\,CN^- + Ag_2S \rightleftharpoons 2\,Ag(CN)_2^- + S^{2-} \tag{8}$$

with $\beta_2 = 10^{20.4}$. If the apparent cyanide response were to be explained by the inherent sulphide response along the same lines that governed the formation of the tricyano–silver complex, a change of 29.6 mV for $\Delta pCN = 1$ and a pH-dependent potential should result. This hypothesis is obviously wrong. If, however, the theory of micro-amounts of free Ag (and S) in silver sulphide is accepted[31], a possible electrode reaction would be:

$$2\,CN^- + Ag \rightleftharpoons Ag(CN)_2^- + e \tag{9}$$

The corresponding electrode potential could be expressed as:

$$E = E^0_{Ag/Ag^+} - 59.2 \cdot \log \beta_2 - 59.2 \cdot \log \frac{[Ag(CN)_2^-]}{[CN^-]^2} \tag{10}$$

If $Ag(CN)_2^-$ at the electrode is formed at a constant rate, establishing a steady-state concentration of the complex, the above electrode reaction should give a change of 118 mV for $\Delta pCN = 1$, which is in relatively good agreement with the experiments at cyanide concentrations below 10^{-2} M, and also in agreement with the value of 103 mV reported for other silver sulphide electrodes[32].

CONCLUSIONS

The electrode potentials can be related to the free silver ion activity, at least in the range 10^{-1}–10^{-24} M Ag^+. The silver sulphide membrane electrodes have a Nernstian response to silver as well as to sulphide ions with a practical limit of detection below 10^{-5} M. The standard potential equals that of a normal silver electrode when the membrane is used with an electrolytic inner contact, but it departs from this value if a metal contact is used.

The influence of moderately interfering ions on the silver or sulphur response of the electrodes agrees with the appropriate solubility products of the sulphide or silver salts of the interfering ions. The electrode is very sensitive to mercury(II) ions, but the potentials are too unstable to be used as a measure for mercury(II) activity. The interference of cyanide with the electrode as a sulphide sensor can be neglected for cyanide concentrations below 10^{-3} M. Above 10^{-2} M cyanide, the response is quasi-Nernstian, and acceptable for analytical purposes.

The manner in which the silver sulphide is precipitated has only a slight influence on the overall electrode properties, but is important for the electrode selectivity obtained.

The electrode potentials are not influenced by light under ordinary laboratory conditions.

SUMMARY

A series of electrodes with membranes of silver sulphide have been prepared. Their standard potentials and their response to sulphide and silver ions are measured and compared with those of a single-crystal silver sulphide electrode. The selectivity parameters against heavy metal ions and halides, as well as cyanide, are discussed. It is concluded that only interferences from cyanide ions and mercury(II) ions are detrimental to the practical use of the electrodes for measuring pAg and pS.

RÉSUMÉ

On a préparé une série d'électrodes avec membranes de sulfure d'argent. Leurs potentiels standards, et leur réponse au sulfure et à l'argent sont mesurés et comparés avec ceux d'une électrode à cristal simple de sulfure d'argent. On examine leurs paramètres de sélectivité contre des métaux lourds et des halogénures, de même que des cyanures. En conclusion, seules les interférences cyanure et mercure(II) sont gênantes pour la mesure de pAg et pS.

ZUSAMMENFASSUNG

Es wurde eine Reihe von Elektroden mit Silbersulfid-Membranen hergestellt. Die Standardpotentiale und das Verhalten gegenüber Sulfid- und Silberionen wurden gemessen und mit jenen einer Einkristall-Silbersulfidelektrode verglichen. Die Selektivitätsparameter gegenüber Schwermetallionen sowie Halogeniden und Cyanid werden diskutiert. Es wird festgestellt, dass nur die Störungen durch Cyanidionen und Quecksilber (II)-Ionen die praktische Anwendung der Elektroden bei der Messung von pAg und pS nachteilig beeinflussen.

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SELECTRODE^{TM}—THE UNIVERSAL ION-SELECTIVE ELECTRODE

PART III. CONCEPT, CONSTRUCTIONS AND MATERIALS

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Ever since the quantitative treatment of electrochemical equilibria was set forth and the potential of electrochemical cells was described by Nernst[1], the importance of electrode properties has been fully realized. In potentiometric analyses both titrations and direct measurements have been studied for decades, but pH measurements were until recently the only direct potentiometric method widely applied in practice. The growth of direct potentiometry only started when attention was turned from glass to other membrane materials like insoluble salts[2] or ion-exchanging liquids immiscible with water[3].

Commercial availability of these electrode types has led to their application in many fields, and has in turn resulted in a growing demand for a new type of sensors with even better selectivities, stabilities etc. Thus, only ten years ago electrodes made of glass, platinum, silver and perhaps mercury were generally applied, while today dozens of chemical compounds are used for making electrodes sensitive to F^-, Cl^-, Br^-, I^-, S^{2-}, NO_3^-, ClO_4^-, CN^-, Ag^+, Na^+, K^+, Cs^+, Pb^{2+}, NH_4^+, Ca^{2+}, Cu^{2+}, Cd^{2+} etc., as well as to biochemically important species.

This rapid and most interesting development has also its particular drawback, as the increase in number of available sensors makes the choice of an electrode for a given task increasingly difficult. Thus, for example, four copper(II)-sensitive electrodes from different manufacturers (Orion, Beckman, Radiometer, Crytur) are commercially available, while six other copper(II) electrodes have recently been reported[4–9]. The membranes of all these electrodes are made in different ways and also of different materials, and therefore their vital properties like stability, selectivity and sensitivity differ considerably. Consequently, a prospective user would tend to test all available types for his particular purpose, but is effectively deterred from doing so by the high cost of commercial sensors (which might run up to half the price of a good pH-meter). Paradoxically, therefore, further introduction of new electrodes appears to hinder their wider practical application.

In this situation the idea of a multipurpose electrode might contribute to further progress. Such an electrode should have a simple, but robust construction, which most importantly would allow the electrode function to be changed at will by renewal of its ion-sensitive surface. This ought to be done in an easy, but strictly

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reproducible manner, and electrode construction should allow use of different electroactive materials. Thus, the electrode function would be either renewed or entirely changed by activating the sensitive surface with different chemical compounds. Therefore the electrode material itself must not take any part in establishing the measured potential, except to serve as inert donor or acceptor of electrons, and it must also be able to accommodate various electroactive materials.

Graphite hydrophobized by teflon is a conductable powder, which is easily compressed at room temperature in virtually any shape. This is the basic material for a new universal ion-selective electrode, the Selectrode[10-13], the potentialities of which are briefly outlined in this paper. The versatility of this electrode is reflected in two ways: by the possibility of varying its electrode function, and by the possibility of varying its physical shape and size according to the desired application.

Basic construction

The basic shape of the selectrode is seen in Fig. 1a, which shows a cylindrical rod (5) pressed of graphite hydrophobized by teflon and mounted in a teflon tube (4) serving as an electrode body. The electrical contact consists of an electrically screened stainless steel wire (2) screwed into the rod. This construction constitutes a basic unit for solid state, liquid state and reference selectrodes.

SOLID-STATE SELECTRODES*

The electrode (Fig. 1a) is activated by:

(a) rubbing of *ca.* 2–4 mg of finely powdered (or colloidal) electroactive material into the electrode surface,

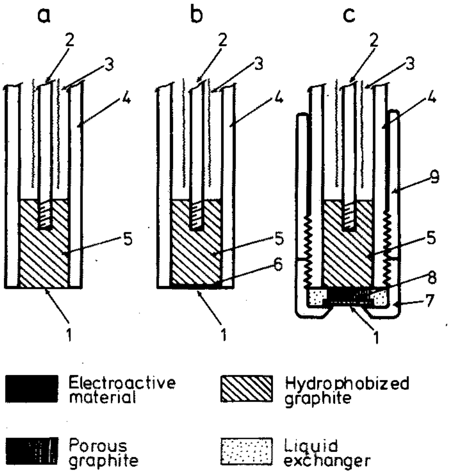

Fig. 1. Selectrode construction. (a) Basic shape: (1) sensitive surface, (2) stainless steel contact, (3) screening, (4) teflon tubing, (5) cylinder pressed from graphite hydrophobized by teflon. (b) Activated solid-state selectrode. The sensitive surface (1) is enriched by electroactive material (6). (c) Activated liquid-state electrode where (7) is the cup, (8) porous pellet and (9) teflon tube with thread.

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* Available from Radiometer A/S, Copenhagen 2400, Denmark.

(b) removing of excessive loose particles,
(c) hand-polishing the electrode surface.

Both hand-polishing and rubbing in are carried out at room temperature. A glass rod, the end of which has been rounded in a flame, can be used for this purpose. The amount of the electroactive material actually embedded in the surface (1) is not critical; for electrodes activated with as little as 1/5 of the indicated quantity still functioned well. Thick layers of electroactive material should, however, be avoided as these are often porous, retain sample solution and therefore slow down the electrode response. As long as the electroactive material is sufficiently conductable, the degree of coverage of the electrode surface is not very critical, hence selectrodes can be prepared in a strictly reproducible manner. As the electroactive material is embedded only in the surface layer (Fig. 1b (1)) the selectrode can easily be "deactivated" by cutting off a thin slice with a lancet, whereupon the freshly cut surface (Fig. 1a (1)) can be activated again. The purpose of the final hand-polishing is to distribute the electroactive material and teflon more evenly over the electrode surface and to close the micropores in the electrode material.

It is difficult to say how long the selectrode would remain activated, because this depends on the properties (mainly solubility) of the electroactive material used. Thus while copper(II) selectrodes, activated by CuS/Ag_2S precipitate lasted more than seven months in continuous use without any change of electrode function, the iodide ion selectrode had to be renewed after only four weeks of operation, and selectrodes employing soluble materials like quinhydrone had to be prepared by a different technique[13].

Redox selectrodes

The redox selectrode was made by rubbing finely powdered, spectrographically pure graphite into the electrode surface. Preliminary experiments indicated that the electrode potential (*E*) measured in redox systems is given by

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Red}]} \tag{1}$$

where E^0 is the standard potential and R, T, n, F have the usual meaning[15], while [Ox] and [Red] represent the activities of an oxidized and reduced form, respectively. The potentials measured by the platinum electrode and by the graphite selectrode showed no significant differences (Table I). The rates of response of the platinum electrode and the graphite-activated selectrode were approximately the same (Fig. 2), due to which the graphite selectrode could be used as indicator in redox titrimetry (Fig. 2a, b).

In this connection it should be mentioned that the "empty" or unactivated selectrode is also redox-sensitive, but the response is much slower and is further substantially delayed by polishing the sensitive surface. Further studies on selectrodes activated by graphite, platinum, gold etc. are still needed in order to reach a better understanding of the redox selectrodes and to confirm these preliminary observations.

Ion-selective selectrodes

The ion-selective selectrodes can be prepared by utilizing various solid materials insoluble in water. Activating the selectrode with powdered or colloidal *metal* yields

TABLE I: USEFUL RANGES, POTENTIALS AND APPLICATIONS OF VARIOUS SELECTRODES

Electroactive material	*Measured ion*	*Useful range pM or pX*	*Solution*	*E mV*	*Potentials (vs. SCE) mV*		*Ref.*	*Analytical application*[h]
					Normal[a] *E′ E″*	*Theoretical*		
Metallic silver	Ag^+	24–1	0.1 *F* $AgNO_3$	+499	+554	+557	(33)	D, T
	Cl^-		0.1 *F* KCl	+45				T
	Br^-		0.1 *F* NaBr	−100				T
	I^-		0.01 *F* NaI	−245				T
	S^{2-}		0.01 *F* Na_2S[b]	−784		−795[b]		T
Metallic copper	Cu^{2+}	3–1			+96	98	(33)	—
CuS/Ag_2S	Cu^{2+}	18–1			+369	+349	(16)	D, T
CdS/Ag_2S	Cd^{2+}	11–1			+100	+83	(16)	D, T
PbS/Ag_2S	Pb^{2+}	~5–1			+100	+130	(16)	T
$AgCl/Ag_2S$	Cl^-	5–1			−12	−20	(33)	D
$AgBr/Ag_2S$	Br^-	6–1			−165	−171	(33)	D, T
AgI/Ag_2S	I^-	7–1			−388	−394	(33)	D, T
$Na[Sb(OH)_6]$	Na^+	~4–1	0.001 *F* NaCl	+111		—	—	—
Quinhydrone[d]	H^+	8–1			+454	+457	(14)	D, T[e]
Thymoquinhydrone[d]	H^+	12–1			+285	—		D, T[e]
Graphite	redox		MnO_4^-/Mn^{2+}	+1206[c]		1258[f]		T
			Ti^{4+}/Ti^{3+}	−243[c]		−243[g]		
Valinomycin	K^+	4.5–1	0.001 *F* KCl	−78		—	—	D
Ca-didecylphosphate	Ca^{2+}	4.5–1	0.001 *F* $CaCl_2$	+185		—	—	D
Ni-bathophenanthroline	NO_3^-	5–1	0.001 *F* $NaNO_3$	+528		—	—	D
Hg/Hg_2Cl_2	reference		KCl (sat)	±0.5		0.0	(14)	R
Ag/AgCl	reference		KCl (sat)– AgCl (sat)	+45		+44	(23)	R
Quinhydrone	reference		Na oxalate– oxalic acid	+299		—	—	—

[a] measured at pM or pX = 3 and extrapolated to pM or pX = 0.
[b] measured at pH = 11.8.
[c] in 1 *F* H_2SO_4.
[d] bulk electrode.
[e] limited life-time.
[f] at pH = 0.
[g] in 0.2 *F* H_2SO_4.
[h] D-direct measurement, T-titration, R-reference electrode.

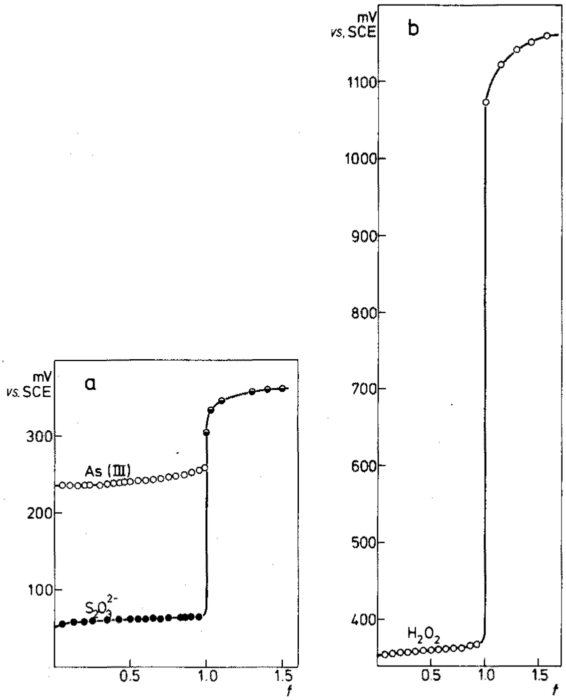


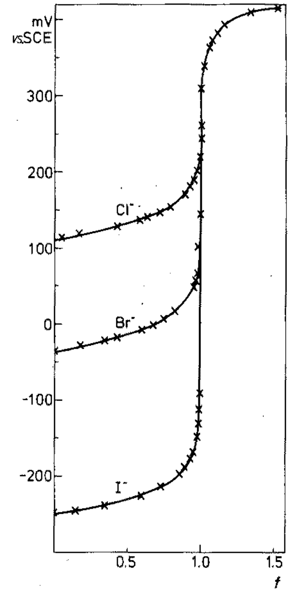
Fig. 2. Potentiometric titrations with redox selectrode, activated by graphite (Spectrographic Carbon Lorraine 208). *f*, titrated fraction. (a) Iodimetric titration of sodium thiosulphate solution (●) and of sodium arsenite solution (○). (b) Titration of hydrogen peroxide by means of cerium(IV) sulphate.

selectrodes equivalent to respective classical metal electrodes. Their potential

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}] \tag{2}$$

is that of a first-kind electrode, reflecting the activity $|M^{n+}|$ of the corresponding metal ion in the solution. This behaviour was observed with selectrodes activated with silver, mercury and copper[11] (Table I), and other metallic selectrodes would probably behave similarly. From an analytical viewpoint, however, only the silver electrode might find wider practical application, as it can be used in the titrimetry of halides (Fig. 3) and possibly also in other potentiometric measurements normally done with the classical silver wire or silver billet electrodes.

Insoluble chemical compounds are the most important electroactive materials, because their use leads to the most selective and sensitive electrodes. Silver halides have been successfully used for making selectrodes sensitive to silver, chloride, bromide and iodide ions[10]. Metal sulphides like HgS, CuS, CdS and PbS have been used to prepare the respective metal ion selectrodes. Of these, however, only the copper(II) selectrode and the cadmium(II) selectrode have been studied in detail[11,12]. It was found that the sensitivities of these electrodes depend entirely on the composition and purity of the electroactive material employed and can be as high as $pCu \approx 18$ and $pCd = 12$, thus reaching the limit imposed by the solubility product of the electroactive compounds ($pS_{CuS} = 34.4$[14], $pS_{CdS} = 25.3$[14] at ionic strength 0.1). The behaviour of



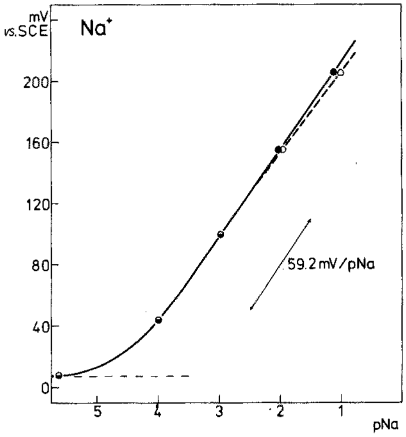


Fig. 3. Potentiometric titrations with silver selectrode, activated by metallic silver. 100.0 ml of $1.00 \cdot 10^{-2}$ *F* of NaI, NaBr or NaCl resp. titrated by means of 0.100 *F* $AgNO_3$ (*f*-titrated fraction).

Fig. 4. Sodium ion solid-state selectrode activated by sodium antimonate (pH 5–6). (●) Activities, (○) concentrations.

these selectrodes can be described by the Nernst equation for cations $[M^{n+}]$:

$$E = E' + \frac{RT}{nF} \ln [M^{n+}] \tag{3}$$

or anions:

$$E = E'' - \frac{RT}{nF} \ln [X^{n-}]$$

depending on the kind of the electroactive material and the composition of the sample solution. The E' and E'' values are interesting not only from a practical, but also from a theoretical viewpoint. For halide selectrodes, these values are in reasonable agreement with those calculated from the standard potential of silver and solubility products of respective halides (Table I). This is, however, not the case with the copper(II) selectrode, when a CuS/Ag_2S precipitate is used as the electroactive material. The electrode exhibited strictly Nernstian response, but its E' value was about 0.265 V more positive than that calculated for a Cu/CuS electrode of the second kind (which is expected to have the same potential as the metallic copper electrode placed in the same solution[15]). This apparent discrepancy has, however, been explained by Sato[16] who concluded that electrodes made of semiconducting binary compounds exhibit a potential which is determined by the composition of the surface region of the electrode material as well as that of the adjacent solution. In these electrodes, the presence of pure metal phase in contact with *e.g.* metal sulphides is not a thermodynamic necessity—a conclusion of obvious importance for the selectrode concept. Remarkably, the potentials of metal sulphide selectrodes (Table I) are in reasonable agreement with the computations of Sato based on solubility products and values of free energies of formation of sulphides.

In this connection the possible use of other chalcogenides as electroactive materials should be mentioned. Thus, electrodes[17] made of Cu_2Se/CuSe proved to be very good sensors for copper(II) ions. The most recent work of Hirata and Higashiyama[9] is concerned with chalcogenide electrodes sensitive to silver, lead, chromium(III), nickel, cobalt(II), cadmium, zinc, copper(II) and manganese ions; these authors used electrodes containing membranes made by compacting and sintering of the corresponding selenides and tellurides mixed with silver sulphide. In analogy with the above-mentioned metal sulphide selectrodes, precipitated mixed chalcogenides should also be useful for activation of the selectrode.

Of other semiconducting inorganic compounds at least one should be mentioned. Sodium antimonate[18] proved to be a suitable material for making a selectrode sensitive to sodium ions (Fig. 4). Although this electrode is also sensitive to other alkali ions (and pH changes), its otherwise satisfactory performance (fast response and stability of potential) indicates the utility of these synthetic inorganic ion exchangers[19] as electroactive compounds.

Another class of compounds, the metal chelates, also seems to be promising for making solid-state selectrodes. From the vast number of these compounds only a few were tested by us. Thus, copper(II) dithizonate and copper(II) diethyldithiocarbamate yielded copper(II) selectrodes with Nernstian response down to *ca.* pCu 8 (at pH 8). Further work on other metal dithizonates, diethyldithiocarbamates and cupferrates is in progress and it is hoped that its results will assist in a more general choice of chelates as electroactive materials.

Yet another class of compounds, the semiconducting organic charge-transfer complexes[5] and ionic radical salts are materials suitable for activation of selectrodes. Wurster salts of the radical cations of derivatives of *p*-phenylenediamine and benzidine were investigated by Sharp[20]; of these, dianisidine perchlorate, N,N,N′,N′-tetramethylbenzidine perchlorate and *o*-dianisidine perchlorate yielded electrodes sensitive to perchlorate ions. The function of the *o*-tolidine perchlorate electrode was explained on the basis of acid–base and redox equilibria.

Quinhydrones have also proved to be useful electroactive materials for making pH-responsive selectrodes. Both quinhydrone and thymoquinhydrone selectrodes behaved theoretically, exhibiting Nernstian response towards hydrogen ions down to the limit imposed by the dissociation of benzoquinhydrone or thymoquinhydrone[13]. Unfortunately, the relatively high solubility of these compounds ($1.8 \cdot 10^{-2}$ mol l^{-1} and $2.8 \cdot 10^{-3}$ mol l^{-1}) necessitated the mixing of the electroactive material with teflon graphite (rather than rubbing it into the surface), which makes these electrodes less practical and prevents change of the electrode function. Moreover their life-time is limited to about one day, after which the electrode surface must be renewed by slicing off a thin layer of electrode material, in order to decrease the response time.

The choice of solid organic and inorganic electroactive materials seems to be very wide, most probably because so little is known about the limiting factors. Low solubility, ion exchange at selective functional groups, and sufficient electrical conductivity are the obvious requirements for the electroactive materials to be used on selectrodes. The electrochemical chain and redox couple involved must also be considered for each electroactive material. However, there are certainly other essential properties, not yet known, and only a systematic study of different compounds will eventually lead to better understanding of all the properties which a suitable electroactive material must possess. Until then the choice will remain a matter of trial and error, complicated by the fact that the method of preparation[11,12] and especially the purity of the precipitate has a profound influence on the sensitivity of the electrode.

In spite of those difficulties the selectrode may at present be activated by various solids, thus becoming selective and theoretically responding towards chloride, bromide, iodide, silver, copper(II) or cadmium(II). The selectrode may also serve as a redox sensor. On the other hand, mercury(II), zinc(II), lead(II)* and sodium selectrodes still have to be developed to a satisfactory level.

LIQUID-STATE SELECTRODES

Successful ion-selective electrodes can also be based on liquid electroactive materials, immiscible with water. These, so-called liquid ion exchangers have been used for making *e.g.* potassium-, calcium- and nitrate-selective liquid–liquid membrane electrodes[3].

These materials might be considered for activation of a selectrode, provided that they could be attached permanently to the graphite surface. The present design (Fig. 1c) originates from the concept of liquid-state electrode[21], and preserves the universality of the selectrode; for again the electrode function can be renewed or entirely changed at will in a simple manner. The body of this electrode (Fig. 1c) is identical with that of the solid-state electrode except that it is furnished with a thread and groove (not shown) on the outside of the teflon tube (4). The groove serves as ventilation for the electrode cavity, which contains a few drops of the liquid, porous pellet (8), and a porous hydrophobized teflon disc (1). The latter two parts are held in position by a teflon cup (7) which is screwed onto the electrode body and secured by a teflon tube (9) which also prevents the ventilation groove from being flooded by the sample solution. Thus the central part of the porous teflon disc (membrane) forms the ion-sensitive part of the electrode and is continuously supplied from within the electrode by organic liquid, as the latter is contained not only in the electrode cavity, but also in the pores of the teflon graphite pellet (8).

When the composition of the organic phase has to be stabilized, this can be done from within the electrode by making the pellet (8) from a mixture of teflon–graphite with a suitable inorganic compound. Similarly, *combinations* of inorganic compounds could be employed and thus a liquid-state selectrode with a "solid-state" inner reference system could be made.

The electrode is activated by soaking both pellet and teflon membrane with an ion exchanger (for *ca.* 10 min in a moderate vacuum) and mounting them. When the electrode is to be renewed, only the teflon disc and the pellet have to be changed. If an entirely different organic liquid is to be used, a thin slice of the teflon graphite rod (5) is sliced off.

In order to test this design, the well studied liquid ion-exchangers 92–20, 92–07 and 92–19 produced by Orion, were applied on the liquid-state selectrode containing the pellet made of teflon·graphite alone. Use of the first liquid, the calcium

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* Lead(II) selectrode has been developed[33].

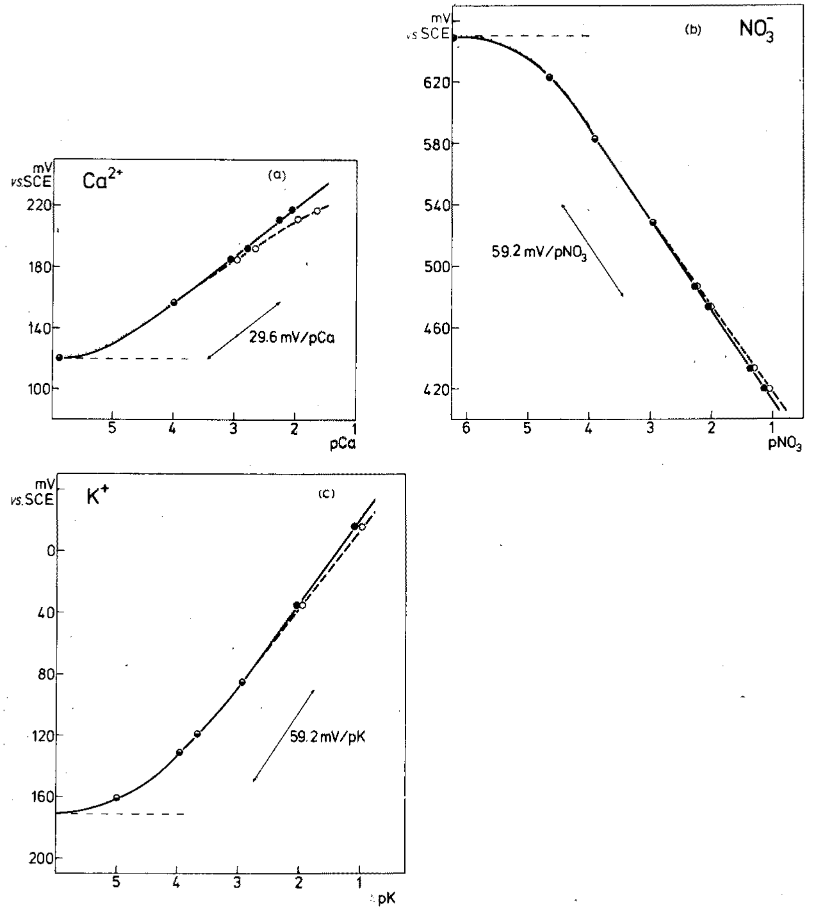

Fig. 5. Liquid-state selectrodes, activated by liquids produced by Orion. (a) Calcium (exchanger 92–20) pH 8–9, pNa 4. (b) Nitrate (exchanger 92–07). (c) Potassium (exchanger 92–19) pH 7–8, pNa *ca.* 4. (●) Activities, (○) concentrations.

salt of didecylphosphoric acid in dioctylphenylphosphonate resulted in a selectrode with a slope close to the Nernstian one and a sensitivity limit of *ca.* pCa 6 (at pH 8.5 and pNa 4) (Fig. 5a). The electrode functioned well over a period of eight weeks without renewing the membrane and its selectivity towards sodium and hydrogen ions was the same as reported for the Orion electrode with the same liquid. Further studies on this calcium electrode are in progress and will be published shortly[22]. The second ion exchanger composed of bathophenanthroline in 2-nitro-*p*-cymol designed for the nitrate-selective electrode, was also found applicable. A nitrate ion selectrode prepared from it (Fig. 5b) exhibited a slope quite close to the theoretical one, but its other parameters still have to be examined. The same applies for the ion exchanging liquid for the potassium-selective electrode, containing valinomycin as the electroactive compound (Fig. 5c).

Although detailed studies of these selectrodes remain to be done, it can already be concluded that the electrode design ensures complete and permanent coverage of the teflon graphite surface with the electroactive material. It is still too early to speculate on the applicability of other organic liquids, but many of those used for solvent extraction of ionic species[23] should be suitable.

REFERENCE SELECTRODES

These electrodes would be in principle the same as the conventional types, *i.e.* of the second kind[15,24]. Consequently, they require solid electroactive materials in combination with the *saturated* solutions of the salts containing the corresponding anion. Thus, the half-cell for the calomel selectrode is

$$\text{C, Hg, Hg}_2\text{Cl}_2\,|\,\text{KCl (sat)}\,||\,\text{sample}$$

and its only novelty is in the electrode design (Fig. 6). The electrode body (4) is the same as that of the liquid-state electrode, again furnished with a thread (but without the ventilation groove) onto which a teflon tube is screwed. The end of this tube is closed by a teflon plug (6) into which has been inserted a cone (7) made of teflon glass. The inner part of the electrode (5) is a cylinder, composed of two layers: one is teflon–graphite, while the other is made from the mixture of the latter with a dry calomel paste (weight ratio 1:1). The electrode cavity is filled with finely milled, solid, wetted potassium chloride.

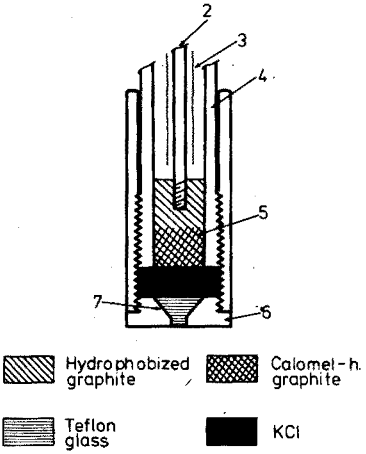

Fig. 6. Reference selectrode. For (2–4) see Fig. 1. (5) is the cylinder composed of two layers, (6) teflon plug containing a cone (7), forming a liquid junction between sample solution and potassium chloride paste.

Of the three main properties of a satisfactory reference electrode: (1) reversibility, (2) reproducibility, (3) stability, only the last two were investigated. This was done by preparing several electrodes and by continuous measurement of their potential *versus* a commercial calomel electrode (Radiometer type 4018) in a solution of 0.1 F sodium nitrate, over a period of several days at a constant temperature ($25 \pm 0.1°$). The largest potential difference observed at the very start of the measurement was 2 mV and after 5 min usually less than 0.5 mV. Later, measured variations of ± 0.1 mV were usually observed. No attempt was made to measure exactly the potential of the calomel selectrode in respect to the hydrogen electrode.

In contrast to commercial electrodes, which are often breakable and invariably of more complicated design, the selectrode can easily be renewed, even if completely dried out. Moreover, when all the potassium chloride has been consumed during use of the selectrode, it can be replenished when the electrode is dismantled. At the same time a thin slice of the inner electrode body (5) can be cut off. During use this inner body is occasionally screwed into the outer tube in order to ensure a slight outflow of the electrolyte into the sleeve junction between (7) and (6). Owing to its robustness, a simplified design of the calomel selectrode has been used for *in situ* measurements in soil[25].

Silver–silver chloride, mercury–mercury(I) sulphate and quinhydrone, oxalic acid–sodium oxalate reference selectrodes were also made and their potentials (Table I) measured. These electrodes could be prepared reproducibly, but they were not further investigated.

DISCUSSION

Although the performance of the many possible selectrodes is the ultimate and significant criterion of the concept of the universal electrode, it cannot be used at this early stage and must be left until detailed studies similar to those performed on copper(II) and cadmium(II) selectrodes have been made. There is, however, another quite important aspect to be discussed, namely, the properties of hydrophobized graphite which make it suitable for ion-selective electrodes.

The use of graphite in electrochemistry has a long tradition, but this material has rarely been considered for electrodes intended for potentiometric measurements. The reasons are the nonideal and poorly reproducible pH sensitivity, and the "memory" of graphite electrodes, which is reflected by irreproducibility of measurements. The reasons for the latter drawback are well known: the pores in the graphite are gradually flooded by the measured solution; when the composition of the sample solution is changed, layers of various compositions accumulate within the electrode body. Thus, although graphite electrodes have been suggested for pH titrations[26,27], they have not found wider application (see Durst[28]).

Graphite exhibits some pH sensitivity because of the presence of chemisorbed oxygen at its surface. While the basal faces of graphite are substantially inert, the edges of the planes are very reactive and form compounds with any suitable foreign atoms present. Oxygen forms acidic surface oxides of carbon, which can be classified as follows: (1) a strongly acidic carboxyl group, (2) a weak acidic group, (3) a phenolic hydroxyl group, (4) a carbonyl group. Their proportion may vary considerably depending on the method of production. Consequently, the pH sensitivities of various carbon electrodes are not comparable. Another important point is that the acidic groups inhibit adsorption of various ionic species from the aqueous solution[29]. Moreover, the presence of oxygen compounds on the graphite surface renders that surface hydrophilic, while graphite free from chemisorbed oxygen is essentially hydrophobic[30]. Thus, graphitized carbon black, Graphon, exhibits a contact wetting angle (θ, for water) of 82°, compared with polyethylene, 94°, and teflon, 108° [31].

The change of hydrophilic to hydrophobic surfaces can, however, be achieved by means of hydrocarbons. Those with short chains yield maximal contact angles of 50–60°, while long chains give contact angles above 100°. The first liquid-state electrode was made of graphite, impregnated by carbon tetrachloride, which made its surface sufficiently hydrophobic to avoid both pH sensitivity and memory effect[21]

The latter effect was eliminated because the graphite pores were filled with organic phase and therefore could not be flooded by sample solution. Later[10], after several compounds had been tested, teflon was adopted. The unactivated, freshly cut or polished selectrode made of this material is not pH-sensitive (Fig. 7a, b), and in contrast to the electrode made of graphite and silicone rubber[32], cannot be made pH-sensitive even by prolonged storage in strong oxidants (Fig. 7c, d). On the other hand, when pyrolytic graphite is used as activator, a typical pH response of a graphite electrode is observed (curve e).

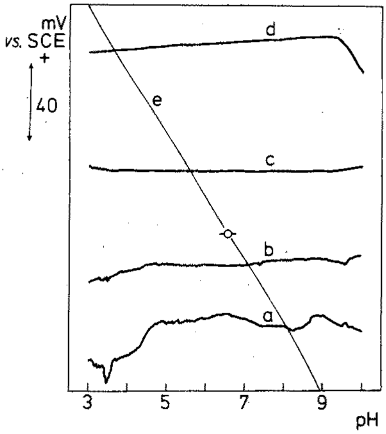

Fig. 7. Influence of pH on the potential of graphite hydrophobized by teflon. (a) Cut selectrode, (b) cut and polished selectrode, (c) as (b), but stored for 3 days in 1 *M* H_2SO_4, (d) as (b), but stored for 3 days in 1 *M* HNO_3–1 *M* $KMnO_4$. Potentials badly reproducible and therefore not stated. (e) Selectrode activated by pyrolytic graphite (Carbon Lorraine V 10). Potentials fairly reproducible (reference point (–○–) at pH 7 equals to +40 mV (SCE)). Average slope of approx. 30 mV/pH. All curves scanned automatically[11,12] from low to high pH at a rate of one pH unit in 2 min starting in 0.001 *F* $NaNO_3$, 0.001 *F* HNO_3 and finishing with 0.002 *F* $NaNO_3$ and 0.0001 *F* NaOH.

The versatility of teflon–graphite also lies in its mechanical properties. The powdered material can be compressed at different pressures, so that bodies of different porosities are obtained. A pressure of 1–2 ton cm^{-2} is suitable for making solid-state selectrodes. Although the material thus prepared is microporous, its surface becomes closed when the electrode is activated, and the remaining pores cannot be flooded with aqueous samples because the material is hydrophobic. The pellet for the liquid-state selectrode is made at a pressure of only about 100 kg cm^{-2}, the porous structure being easily impregnated by organic liquid. When even greater porosity is required (see reference selectrodes), finely pulverized water-soluble salts can be milled together with teflon graphite in weight ratios up to 1:1 and then compressed to the required shape. Various mixtures of teflon–graphite, pure teflon powder and other materials can be conveniently formed into different physical shapes, so that flow-through types or microelectrodes can be constructed.

CONCLUSION

The renewed interest in potentiometry is due to the fact that new electroactive materials have been recognized and employed for making ion-selective electrodes. Thus, new fascinating chemical aspects have been brought into this traditional field of analytical research. Unfortunately, quite sophisticated methods are usually necessary to produce electrodes, and much still remains proprietary information. Consequently, each electrode type has been considered as a separate species, which makes comparison and application of electrodes more difficult as their variety and number increase. If this trend continues, a laboratory should be equipped with dozens of sensors, which is neither practical nor economical.

The results summarized here confirm the possibility of making a universal electrode, which can in turn accommodate various electroactive materials. Presently, about half a dozen materials are available each of which may activate the selectrode to exhibit the selective Nernstian response. Although some materials (*e.g.* glass and lanthanum fluoride) cannot be used, the choice of suitable compounds seems to be rather wide, and future developments should be extensive.

We wish to express our thanks to Professor N. Hofman-Bang for his support, to E. H. Hansen for a number of discussions, to T. Frederiksen and G. Møller for technical assistance and to O. J. Jensen from Radiometer A/S (Copenhagen) for critical cooperation.

SUMMARY

The concept and construction of a multipurpose electrode, the selectivity of which can easily be changed, is described. The change of electrode response is achieved by using various electroactive materials, which can be either solid (solid-state selectrode) or liquid (liquid-state selectrode). A number of electroactive materials is discussed and sensitivities and characteristic potentials of various selectrodes are given. A reference selectrode which employs a humidified solid salt instead of the saturated solution of an electrolyte is also described.

RÉSUMÉ

On propose une électrode à emplois multiples, avec sélectivité facilement modifiable. Le changement de réponse est réalisé au moyen de diverses sélectrodes, solides ou liquides. On décrit également une sélectrode de référence, utilisant un sel solide humidifié, au lieu d'une solution saturée d'électrolyte.

ZUSAMMENFASSUNG

Das Prinzip und der Aufbau einer Vielzweckelektrode, deren Selektivität leicht geändert werden kann, werden beschrieben. Die Änderung im Ansprechen der Elektrode wird durch Verwendung verschiedener elektroaktiver Substanzen erreicht, die entweder fest (Festkörper-Selektrode) oder flüssig (Flüssigkeits-Selektrode) sein können. Eine Anzahl elektroaktiver Substanzen wird diskutiert, und die Empfindlichkeiten und charakteristischen Potentiale verschiedener Selektroden werden angegeben. Eine Referenz-Selektrode, die an Stelle der gesättigten Lösung eines Elektrolyten ein angefeuchtetes festes Salz enthält, wird ebenfalls beschrieben.

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PREPARATION AND ANALYTICAL EVALUATION OF A NEW THIOCYANATE SOLID-STATE HETEROGENEOUS MEMBRANE ELECTRODE*

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Thiocyanate solid-state electrodes have been reported by Ross[1]; silver sulphide and silver thiocyanate in very finely divided form were mixed and pressed to obtain a homogeneous polycrystalline membrane. The detailed behaviour of this Orion electrode does not seem to have been investigated.

This paper describes the preparation of a heterogeneous thiocyanate membrane electrode made with crystalline material and with a thermoplastic polymer, *e.g.* polythene or metacrylic esters, its analytical response in aqueous and non-aqueous solvents and its application in complex chemistry.

EXPERIMENTAL

The silver salts used in the preparation of membrane electrodes were obtained as follows: (a) by precipitation of silver thiocyanate; (b) by precipitation of silver thiocyanate mixed with silver sulphide.

The membrane electrode was prepared as described previously[2]. The mixture of silver salts was thermomoulded with a thermoplastic polymer such as polythene. The membranes obtained, which were 1–2 mm thick and 12 mm in diameter, were thermosealed in a suitable mould to a rigid polythene tube. When this procedure was used, the electrodes had good mechanical properties and chemical durability as no adhesives were required. The electrodes were well suited for use in non-aqueous solvents.

The internal solution was 10^{-3} *M* silver nitrate; a silver wire, dipped into it, was thermosealed to the polythene tubing and acted as an internal reference electrode.

Potentiometric measurements were carried out in the conventional manner by using the membrane electrode and a saturated calomel electrode as a reference with a Beckman Research pH meter 1019. Potentiometric titrations were performed in stirred solutions. The titrations in non-aqueous media were performed with the reagents dissolved in the appropriate solvent.

RESULTS AND DISCUSSION

Membrane electrodes prepared from the silver salts described above, were silver- and thiocyanate-selective electrodes. Calibration curves obtained by plotting E *vs.* log $[SCN^-]$ and *vs.* log $[Ag^+]$ showed that the difference between the two kinds

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of membrane electrode was not relevant. No photoelectric effect was noticed with the silver thiocyanate membranes.

In the following studies only the electrodes obtained from silver thiocyanate precipitates were used. A set of 20 electrodes was tested; all yielded reproducible results, the behaviour of any single electrode deviating from the average value by not more than 2–3 mV.

Response of electrode to silver ion activity

To evaluate the response of this electrode toward changes in silver ion, the following cell was used:

$$\text{S.C.E.} \mid 1\ M\ \text{NaNO}_3 \mid \text{Ag}^+\ \mu=0.1\ (\text{NaNO}_3) \mid \text{AgSCN electrode}$$

The e.m.f. is given by the Nernst relationship

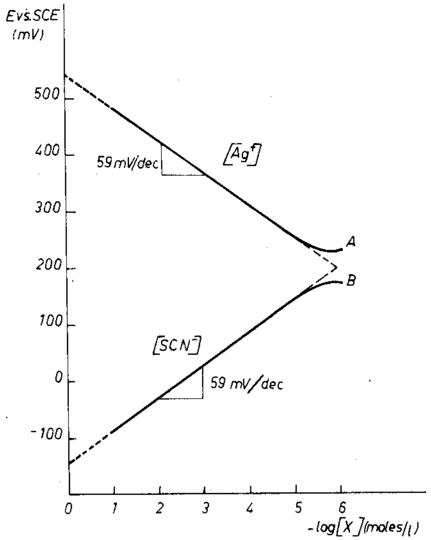
$$E = \text{E}^0 + 0.059 \log\,[\text{Ag}^+] \qquad (1)$$

where the E^0 term includes the potential of the internal electrode, the reference electrode, the liquid junction and the activity coefficient for silver ion. The plot of E *vs.* log $[\text{Ag}^+]$ is shown in Fig. 1; the slope is 59 mV per decade change in concentration. Extrapolation to $[\text{Ag}^+]=1$ gives the normal potential of the membrane electrode, $E^0=540$ mV, which is in good agreement with e.m.f. of other silver membrane electrodes[2] (E^0 for Ag/Ag$^+$ is 558 mV).

Like the silver sulphide membrane electrode, which is considered the best silver electrode, the thiocyanate electrode has a sensitivity limit which is in theoretical agreement with its higher solubility product. At 10^{-5} M silver concentration. the calibration curve deviates from linearity.

Response of electrode to thiocyanate ion activity

If the original sample contains no silver ions, but thiocyanate, the resulting



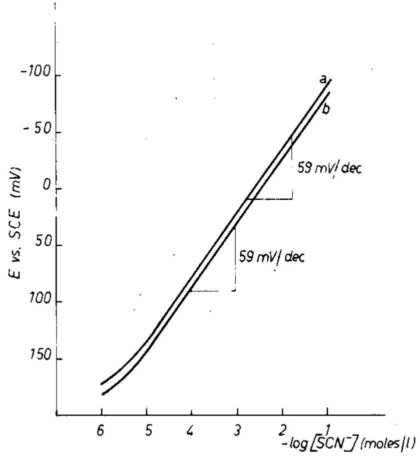


Fig. 1. Calibration curves for the thiocyanate electrode at ionic strength 0.1 *M*.

Fig. 2. Effect of ionic strength. (a) Calibration curve in aqueous solution; (b) at ionic strength 1 *M*.

silver ion activity will depend on the thiocyanate activity and eqn. (1) becomes

$$E = E^0 + 0.059 \log K_{so} - 0.059 \log [SCN^-] \tag{2}$$

The plot of E *vs.* log $[SCN^-]$ is shown in Fig. 1. The potential intercept, obtained by extrapolating to $[SCN^-] = 1$, gives a value from which the solubility product of silver thiocyanate can be calculated.

A value of $10^{-11.8}$ was obtained; values from $10^{-12.1}$ to $10^{-11.1}$ have been reported[3].

Effect of pH

The influence of pH on the potential of these electrodes was investigated. The potential of the electrodes was measured in solutions of pH varying in the range 1–13 in the presence of an inert electrolyte to maintain constant ionic strength and in the presence of 10^{-3} *M* thiocyanate. No variation of potential was noted.

Effect of ionic strength

Ionic strength affects the potential value by varying the activity coefficient of thiocyanate. In Fig. 2 calibration curves are plotted at different ionic strengths. The difference of the two calibration curves is 5–6 mV.

Electrode selectivity

The effect of various anions on the response of the silver thiocyanate membrane electrode was determined by the e.m.f. values of the cell with the indicator electrode placed in solutions containing a fixed concentration of interfering ion and varying concentrations of thiocyanate.

Figure 3 shows the deviation of the calibration curve from linearity in the presence of iodide, bromide and chloride, all of which react with the precipitate and so interfere in the measurement. The interferences, as expected from the K_{so} values, are in the following order $I^- > Br^- > Cl$.

In order to evaluate the extent of the interference, the following equation[1] was applied:

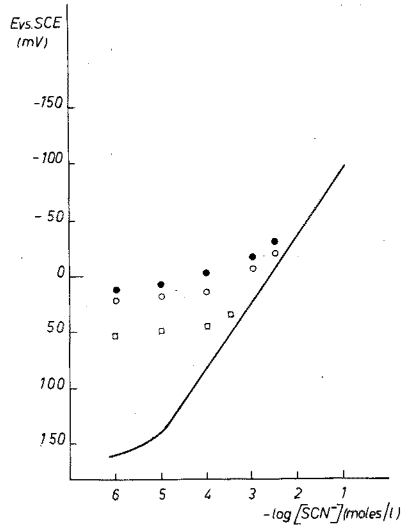
$$E = E^0 - 0.059 \log (a_1 + K_{12} \cdot a_2)$$

where a_1 is the activity of the thiocyanate and a_2 the activity of the interfering ion; K_{12} is the selectivity constant. The K_{12} values were calculated by comparing the potentials measured in a solution of thiocyanate at various concentrations, with and without interfering ions. The values are reported in Table I.

TABLE I

K_{12} VALUES MEASURED FOR DIFFERENT THIOCYANATE CONCENTRATIONS WITH INTERFERING IONS IODIDE, BROMIDE AND CHLORIDE

$[SCN^-]$	10^{-5} *M*	10^{-4} *M*	10^{-3} *M*
0.1 *M* $[Cl^-]$	$2.8 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	—
10^{-3} *M* $[Br^-]$	1.0	1.4	1.6
10^{-5} *M* $[I^-]$	$1.7 \cdot 10^2$	$2.7 \cdot 10^2$	$4.7 \cdot 10^2$



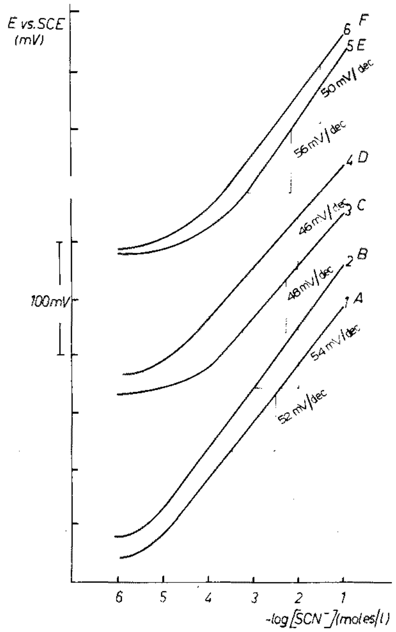


Fig. 3. Effect of iodide, bromide and chloride. (—) Calibration curve without interference; (●) with 10^{-5} M iodide; (○) with 10^{-3} M bromide; (□) with 10^{-1} M chloride.

Fig. 4. Calibration curves in different solvents. (A) 100% acetone; (B) 50% acetone at ionic strength 0.1 (KNO_3); (C) 100% acetonitrile; (D) 50% acetonitrile at ionic strength 0.1 (KNO_3); (E) 100% methanol; (F) 50% methanol at ionic strength 0.1 (KNO_3).

Direct potentiometry in mixed and in non-aqueous solvents

Measurements of thiocyanate by direct potentiometry in water–acetone, water–methanol and water–acetonitrile mixtures and in pure acetone, methanol, and acetonitrile are shown in Fig. 4. Approximate Nernstian response to thiocyanate concentrations at constant ionic strength was observed in the range 0.1–10^{-4} M.

Figure 4 indicates that a different calibration curve is necessary for each solvent mixture.

Studies of thiocyanate equilibria

The thiocyanate ion reacts with several ions in aqueous and non-aqueous media to form precipitates and complexes. The membrane electrode was tested as an end-point indicator for these reactions.

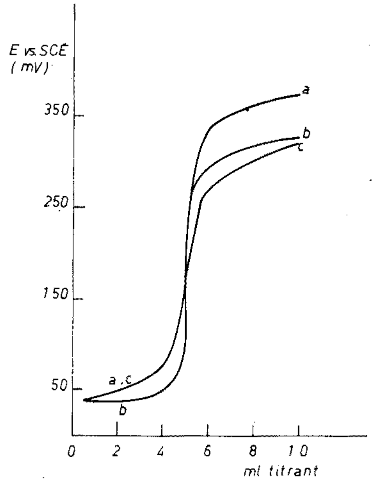
The potentiometric titrations of thiocyanate with silver(I), mercury(I) and mercury(II) in aqueous solution are shown in Fig. 5. The reactions considered are as follows:

$$Ag^+ + SCN^- \rightleftharpoons \mathit{AgSCN}\ ;\ pK = 12$$

$$Hg_2^{2+} + 2\ SCN^- \rightleftharpoons \mathit{Hg_2(SCN)_2}\ ;\quad pK = 19.5$$

$$Hg^{2+} + 2\ SCN^- \rightleftharpoons \mathit{Hg(SCN)_2}\ ;\quad pK_1 + pK_2 = 17.5$$

The curves show large potential variations at the equivalence point and the potential



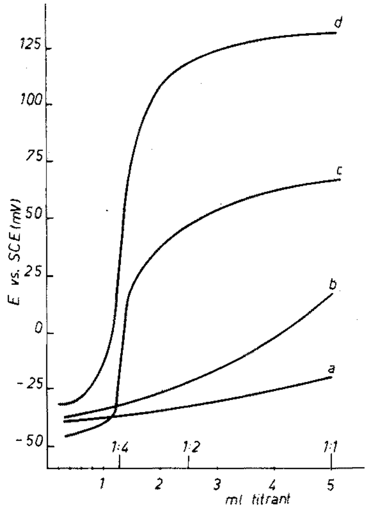
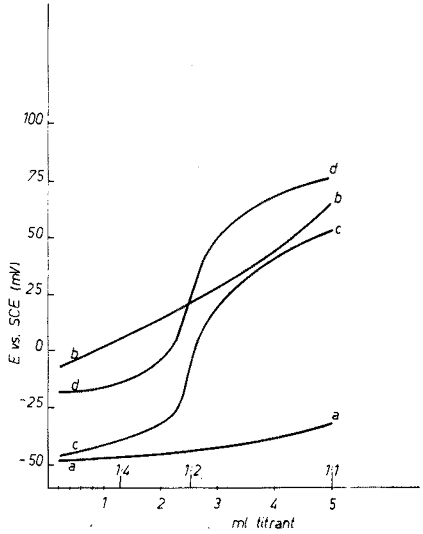


Fig. 5. Titration curves in aqueous solutions. 50 ml of 10^{-3} M KSCN are titrated with (a) 10^{-2} M $AgNO_3$; (b) 10^{-2} M $Hg_2(NO_3)_2$; (c) 10^{-2} M $Hg(NO_3)_2$.

Fig. 6. Potentiometric titrations of 10^{-2} M KSCN with 10^{-1} M $Co(NO_3)_2$ in (a) water, (b) methanol, (c) acetonitrile, (d) acetone.



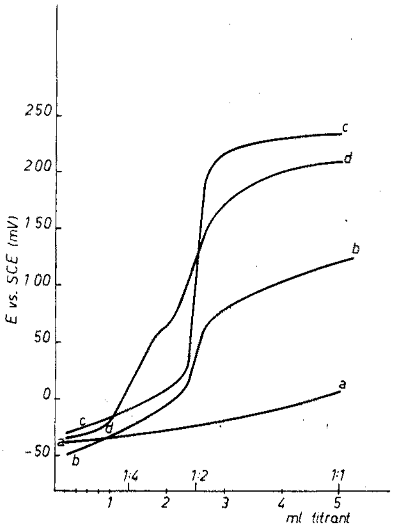
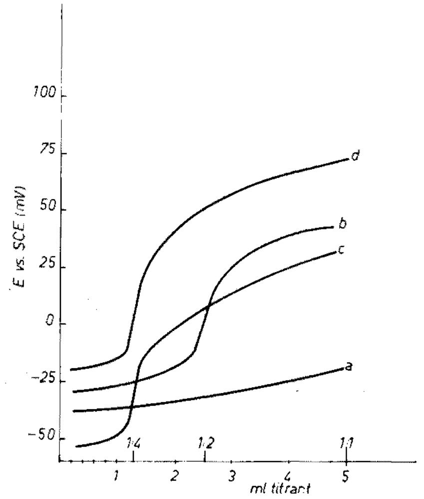


Fig. 7. Potentiometric titrations of 10^{-2} M KSCN with 10^{-1} M $Ni(NO_3)_2$ in (a) water, (b) methanol, (c) acetonitrile, (d) acetone.

Fig. 8. Potentiometric titrations of 10^{-2} M KSCN with 10^{-1} M $Cu(NO_3)_2$ in (a) water, (b) methanol, (c) acetonitrile, (d) acetone.

jump is related to the stability constant value.

Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Fe^{3+} are reported to form weak complexes with thiocyanate in aqueous solution. The formation of these complexes in aqueous and non-aqueous media was compared, and the results are shown in Figs. 6–10. The breaks obtained are quite large in acetonitrile and acetone and permit the determination of the metallic ions in these media. Rapid semiquantitative information can be obtained on the p*K* values in the different media.



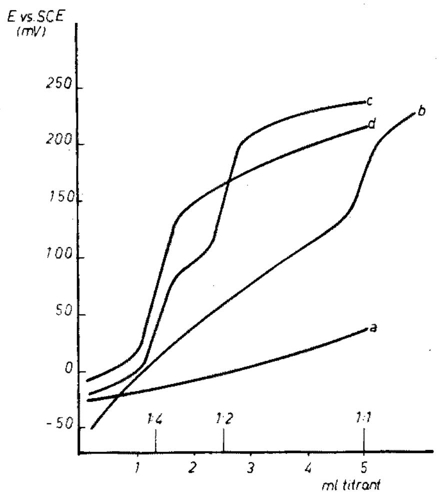


Fig. 9. Potentiometric titrations of 10^{-2} *M* KSCN with 10^{-1} *M* $Cd(NO_3)_2$ in (a) water, (b) methanol, (c) acetonitrile, (d) acetone.

Fig. 10. Potentiometric titrations of 10^{-2} *M* KSCN with 10^{-1} *M* $Fe(NO_3)_3$ in (a) water, (b) methanol, (c) acetonitrile, (d) acetone.

The chemistry of the tested systems in the various media can be illustrated by the following equations:

$Co^{2+} + 4\,SCN^- \rightleftharpoons Co(SCN)_4^{2-}$ in acetonitrile and in acetone

$Ni^{2+} + 2\,SCN^- \rightleftharpoons Ni(SCN)_2$ in acetonitrile and in acetone

$Cu^{2+} + 2\,SCN^- \rightleftharpoons Cu(SCN)_2$ in methanol, acetonitrile and acetone

$Cu^{2+} + 4\,SCN^- \rightleftharpoons Cu(SCN)_4^{2-}$ only in acetone

$Cd^{2+} + 2\,SCN^- \rightleftharpoons Cd(SCN)_2$ in methanol

$Cd^{2+} + 4\,SCN^- \rightleftharpoons Cd(SCN)_4^{2-}$ in acetonitrile and in acetone

$Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+}$ in acetone

$Fe^{3+} + 2\,SCN^- \rightleftharpoons Fe(SCN)_2{}^+$ in acetonitrile

$Fe^{+3} + 4\,SCN^- \rightleftharpoons Fe(SCN)_4{}^-$ in acetonitrile and in acetone

Kinetic studies

As an application of the thiocyanate electrode, the kinetic constant of the following reaction[4]:

$$Co(NH_3)_5\,SCN^{2+} + OH^- \rightleftharpoons Co(NH_3)_5OH^{2+} + SCN^-$$

was determined. The nitrate salt of the thiocyanate complex was obtained as described in the literature[4].

If $[OH^-]$ is constant, the reaction rate depends only on $[Co(NH_3)_5\,SCN^{2+}]$ and if $x = [Co(NH_3)_5\,SCN^{2+}]$ we have:

$$-dx/dt = Kx$$

$$K = -(\log x + \text{const})/t$$

where $x = a - [SCN^-]$, a = initial concentration of $Co(NH_3)_5\,SCN^{2+}$, and const $= -\log x\,(t=0) = -\log a$.

The thiocyanate concentration was followed with the membrane electrode; a was established by a determination of cobalt. The E *vs.* time plots for three experiments in which the concentrations of $Co(NH_3)_5SCN^{2+}$ were $8.8 \cdot 10^{-3}$, $4.4 \cdot 10^{-3}$ and $2.2 \cdot 10^{-3}$ M with a hydroxide concentration of 0.5 M are shown in Fig. 11. Log x *vs.* time plots are also given. From the slope, the kinetic constant $K = 4.3 \cdot 10^{-4}$ s^{-1} was calculated.

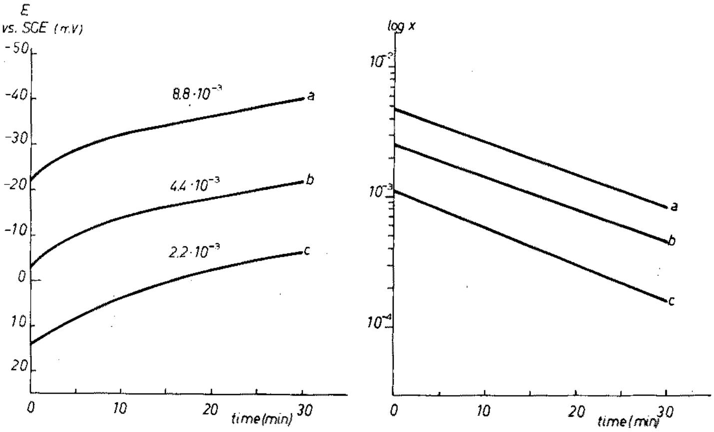


Fig. 11. Hydrolysis of $Co(NH_3)_5SCN^{2+}$ in 0.5 M NaOH. From the plot of E *vs.* time, the plot log x *vs.* time was calculated; $K = 4.3 \cdot 10^{-4}$ s^{-1}

The applications reported above for the thiocyanate heterogeneous membrane electrode show how it can be employed in different fields of analytical chemistry in aqueous and non-aqueous media to elucidate thiocyanate chemistry.

SUMMARY

Silver thiocyanate mixed with thermoplastic polymers and thermomoulded in a suitable press forms a membrane electrode selective to thiocyanate and silver ions. The analytical behaviour of this electrode is described in terms of potential–activity curves, standard potential, electrode selectivity with halide ions, and behaviour in non-aqueous solvents. Several titrations in aqueous and non-aqueous media were done to evaluate the performances of the new electrode. The electrode was used to study the kinetics of the alkaline hydrolysis of a thiocyanate complex, $Co(NH_3)_5SCN^{2+}$

RÉSUMÉ

Une étude est effectuée sur les électrodes au thiocyanate. On décrit la préparation d'une électrode à membrane hétérogène avec matériel cristallisé et polymère thermoplastique, par exemple esters métacryliques ou polythène. On examine son comportement, sa réponse analytique en solvants aqueux et non aqueux, de même que ses possibilités d'application dans la chimie des complexes.

ZUSAMMENFASSUNG

Silberthiocyanat, das mit thermoplastischen Polymeren gemischt und in einer geeigneten Presse unter Wärmeeinwirkung gepresst wird, ergibt eine für Thiocyanat- und Silberionen selektive Membranelektrode. Das analytische Verhalten dieser Elektrode wird beschrieben hinsichtlich Potential–Aktivitäts-Kurven, Standardpotential, Elektrodenselektivität gegenüber Halogenidionen und Verhalten in nichtwässrigen Lösungsmitteln. Die Leistungsfähigkeit der neuen Elektrode wurde durch verschiedene Titrationen in wässrigen und nichtwässrigen Systemen belegt. Die Elektrode wurde auf die Untersuchung der Kinetik der alkalischen Hydrolyse des Thiocyanatkomplexes $Co(NH_3)_5SCN^{2+}$ angewendet.

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MEASUREMENT OF ORGANIC ACIDS WITH A N-SILICON SEMICONDUCTOR ANODE

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Since the introduction of the low-resistivity N-silicon anode as an acid sensor in 1970[1], the applications have mainly been to measurements of inorganic acids in industrial metal treating baths. Yang[2] measured hydrofluoric acid in mixed nitric acid–hydrofluoric acid baths used for titanium pickling, while McKaveney[3] extended the hydrofluoric acid measurements to mixtures with sulfuric and phosphoric acids. Straub *et al.*[4] recently discussed their detailed work on the application of the N-silicon anode to the measurement of hydrofluoric acid in mixed nitric–hydrofluoric acid stainless steel pickling baths as well as to the measurement of hydrochloric and sulfuric acid in the respective carbon steel pickling baths. They also used the electrode for the measurement of phosphoric acid in phosphate–chromate steel treating baths.

In the earlier publication[1], a very brief indication was given of the response of the N-silicon anode to selected organic acids of about 0.010 *N* concentration. The data indicated that at the concentrations examined certain of the acids (oxalic and tartaric) responded similarly to strong acids, *e.g.* sulfuric acid, while acetic and citric acids responded as very much weaker acids. This investigation was undertaken to extend the earlier work with organic acids and hopefully to find a more efficient procedure for their measurement than the presently used titration methods[5,6].

EXPERIMENTAL

Reagents

Acetic acid, 0.100 N. Transfer 5.80 ml of anhydrous acetic acid to a 1-l volumetric flask and dilute to volume.

Citric acid, 0.100 N. Transfer 6.404 g of reagent-grade crystals (m.w. = 192.13) to a 400-ml beaker containing 200 ml of water. After dissolving, transfer with washing to a 1-l volumetric flask and dilute to volume.

Tartaric acid, 0.100 N. Dissolve 7.500 g of crystals (m.w. = 150.09) in 300 ml of distilled water. Transfer with washing to a 1-l volumetric flask and dilute to volume.

Oxalic acid, 0.100 N. Dissolve 6.304 g of oxalic acid dihydrate (m.w. = 126.07) in 300 ml of water using a low heat hot plate. Cool, transfer to a 1-l volumetric flask with washings and dilute to volume.

Dilute acids, 0.010–0.050 N. Transfer 10, 20, 30, 40 and 50-ml volumes of the respective 0.100 *N* acids to 100-ml plastic volumetric flasks. Add 5.0-ml volumes of ammonium fluoride solution (220 g l^{-1}) and dilute to 100 ml with water. These solutions are used for the experimental calibration curves.

Apparatus

Acid concentration meter, Type ACM-1 (Beckman Instruments, Inc., Cedar Grove, N.J.). The instrument contains a $\frac{3}{16}$-in diameter slice of low resistivity N-silicon as the anode surrounded by a $\frac{3}{8}$-in o.d. stainless steel cathode tube of $\frac{1}{32}$-in thickness. Both battery and 120/240 V power options are available to cover the meter scale range from 0.001 to 0.050 *N* in acid concentration. A thermometer (0–60.0°) is fitted into one slot of the electrode holder and is used in conjunction with the temperature compensator.

Procedure

Transfer a 100-ml volume of 0.050 *N* acid containing 1.10 g of ammonium fluoride to a 150-ml black plastic beaker. Add a magnetic stirring bar, and stir the solution at a moderate speed. Insert the combination electrode and thermometer so that both are about 1 cm above the stirrer. With the power on, read the thermometer and set the temperature compensation control to the measured temperature. Adjust the standardization control to obtain full-scale deflection (0.050 *N*). After standardizing, measure the concentration of each acid from 0.010 to 0.040 *N* and record the meter readings. The most critical step of the measurement involves adjustment of the temperature compensation knob for any noticeable changes in temperature.

RESULTS AND DISCUSSION

The data recorded for the various acids when hydrochloric acid was used to calibrate the instrument, are shown in Table I. It is obvious that none of the acids produces a linear response under these conditions. The calibrating hydrochloric acid approaches linearity above 0.030 *N*. The highest values of the respective acids for the 0.050 *N* level from acetic at 0.0143 to oxalic at 0.0360 reflect the gradations in

TABLE I

RESPONSE OF ORGANIC ACIDS WITH AN N-SILICON/STAINLESS STEEL ELECTRODE[a]

Acid concentration[b] *(N)*	*Acid, meter reading*				
	Acetic	*Citric*	*Oxalic*	*Tartaric*	*Hydrochloric*
0.0100	0.0045	0.0054	0.0070	0.0071	0.0072
0.0200	0.0078	0.0093	0.0140	0.0139	0.0160
0.0300	0.0105	0.0130	0.0215	0.0204	0.0272
0.0400	0.0125	0.0171	0.0305	0.0271	0.0391
0.0500	0.0143	0.0215	0.0360	0.0326	0.0500 (calibrate)

[a] N-Si/stainless steel combination electrode calibrated to 0.0500 *N* with 0.0500 *N* hydrochloric acid.
[b] Measurement on 100 ml of acid containing 5 ml of ammonium fluoride solution (1.10 g) as electrolyte at 25.0°.

their acid strengths compared to hydrochloric acid. At the more dilute 0.010 *N* level, it is interesting to note that oxalic, tartaric and hydrochloric acid all have nearly the same meter response of about 0.0071. This is in accord with the earlier report that acid dilution causes these organic acids to approach complete ionization in the ammonium fluoride electrolyte.

It should be recalled that the N-silicon anode is a selective monitor for hydrofluoric acid, and the principal purpose of the ammonium fluoride is to transform all the acids to hydrofluoric acid. Earlier data indicated that all acids with K_{ion} values greater than that of hydrofluoric acid ($7.2 \cdot 10^{-4}$) produced the same response at a fixed concentration with the N-silicon anode.

TABLE II

CALIBRATION DATA FOR ORGANIC ACIDS WITH N-SILICON/STAINLESS STEEL ELECTRODE[a]

Acid concentration[a] *(N)*	*Acid, meter reading*				
	Acetic	*Citric*	*Oxalic*	*Tartaric*	*Hydrochloric*
0.0100	0.0153	0.0120	0.0097	0.0098	0.0072
0.0200	0.0262	0.0220	0.0199	0.0200	0.0160
0.0300	0.0353	0.0310	0.0305	0.0309	0.0272
0.0400	0.0422	0.0410	0.0401	0.0405	0.0391
0.0500	0.0500	0.0500	0.0500	0.0500	0.0500

[a] N-Si/stainless steel electrode calibrated to 0.0500 *N* with each respective acid containing 1.10 g NH_4F/100 ml as electrolyte at 2.50°.

The next experiment (Table II) involved separate calibrations for each of the acids used, *i.e.*, the 0.050 *N* concentration levels of the respective acids were used to set the calibrations. These data were much more satisfactory; citric, oxalic and tartaric acids exhibited nearly linear response. Acetic acid at the more dilute level (0.010 *N*) was very sensitive but levelled off from linearity above 0.025 *N*. The data for hydrochloric acid are the same as in Table I and are listed for comparison purposes.

It is apparent that the standardization control on the commercial instrument is an asset over the earlier manual model[1] which limited the organic acids to the lower meter ranges. Thus, organic commercial products such as vinegar or cellulosic by-products (acetic acid), lemon juice (citric acid) and wine (tartaric acid) should be suitable for use with the N-silicon anode. From a theoretical standpoint, the linearity of oxalic and tartaric acids in particular may be related to their average K_{ion} values approaching that of hydrofluoric acid. Also as noted in the earlier paper[1], there may be a relationship for these acids between the anodic response and their complexing ability for silicon.

The data given in Table III indicate the pH response for two concentration levels of the acids examined. The pH and ionization constant values follow the expected pattern with the ΔpH values showing the greatest spread for the stronger acids. A comparison of these data with those of Table I shows the same general agreement regarding acids strength, *i.e.*, hydrochloric > oxalic > tartaric > citric > acetic.

TABLE III

DATA FOR pH AND IONIZATION OF ORGANIC ACIDS[a]

Acid	*Normality*	*pH*	*ΔpH*	K_{ion}
Acetic	0.0100	3.38		
	0.0500	2.98	0.40	$1.753 \cdot 10^{-5}$
Citric	0.0100	2.85		$8.7 \cdot 10^{-4}$ K_1
	0.0500	2.46	0.39	$1.8 \cdot 10^{-5}$ K_2
				$4.0 \cdot 10^{-6}$ K_3
Tartaric	0.0100	2.73		$9.6 \cdot 10^{-4}$ K_1
	0.0500	2.30	0.43	$2.9 \cdot 10^{-5}$ K_2
Oxalic	0.0100	2.33		$5.9 \cdot 10^{-2}$ K_1
	0.0500	1.74	0.59	$6.4 \cdot 10^{-5}$ K_2
Hydrochloric	0.0100	2.03		
	0.0500	1.31	0.72	

[a] pH meter calibrated with pH 4.00 buffer.

TABLE IV

SENSITIVITY TO TEMPERATURE OF THE N-Si/STAINLESS STEEL COMBINATION ELECTRODE

Temperature (°)	*Meter reading*	*Δ Meter*
20.0	0.0339	
21.0	0.0354	0.0015
22.0	0.0370	0.0016
23.0	0.0386	0.0016
24.0	0.0403	0.0017
25.0	0.0420	0.0017
26.0	0.0438	0.0018
27.0	0.0457	0.0019
28.0	0.0477	0.0020
29.0	0.0500[a]	0.0023
30.0	0.0522[b]	0.0022

[a] Meter calibrated at 29.0° with 0.0500 *N* tartaric acid containing 1.10 g NH_4F per 100 ml.
[b] Extrapolated value from data plot.

One import aspect of the meter operation is the necessity of temperature correction for accurate measurements. The data of Table IV illustrate this fact. The particular calibration was prepared from a 0.050 *N* tartaric acid solution at 29.0° and the solution was allowed to cool while data were recorded. On reheating the solution from 20° to 29.0°, the data were almost exactly reproduced. An error of ±4% was found for each degree difference from calibration, unless the temperature compensation control was used.

In conclusion, the N-silicon/stainless steel combination electrode appears applicable to the determination of water-soluble organic acids having K_{ion} values greater than $1 \cdot 10^{-6}$. The method has an advantage over the conventional alkali titration procedure in that the usual problems arising from carbon dioxide absorption or ester hydrolysis do not occur. Moreover, no difficulties are encountered with turbid or colored solutions which normally require a potentiometric titration. The combination electrode is sturdier than the conventional glass and calomel electrodes, and, of course, there are no problems of locating the exact end-points for titrations of organic acids with alkali.

SUMMARY

A combination N-silicon/stainless steel electrode is suitable for the measurement of water-soluble organic acids with K_{ion} values exceeding $1 \cdot 10^{-6}$. A commercial acid concentration meter was used for the measurements; the standardization control permits a nearly linear response to the acids over the range 0.001–0.050 *N*. Because of the semiconductor temperature sensitivity, precise measurements require the use of temperature compensation. The combination electrode eliminates the problems found routinely with the standard alkali titration.

RÉSUMÉ

On propose une électrode spéciale pour la détermination d'acides organiques solubles dans l'eau avec K_{ion} supérieur à $1 \cdot 10^{-6}$. Cette électrode permet d'éviter les difficultés rencontrées au cours d'un titrage avec alcali standard.

ZUSAMMENFASSUNG

Eine Kombinationselektrode aus N-Silicium und Edelstahl eignet sich für die Messung wasserlöslicher organischer Säuren mit K_{ion} Werten grösser als $1 \cdot 10^{-6}$. Für die Messungen wurde ein handelsüblicher Säurekonzentrationsmesser verwendet; die Standardisierungskontrolle ermöglicht ein nahezu lineares Ansprechen auf Säuren im Bereich 0.001–0.050 *N*. Wegen der Temperaturempfindlichkeit des Halbleiters erfordern genaue Messungen eine Temperaturkompensation. Die Kombinationselektrode schaltet die Probleme aus, die gewöhnlich bei der Standardalkalititration auftreten.

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STABILITY CONSTANTS OF SOME STERICALLY HINDERED BIS-(8-QUINOLINOLATO)COPPER(II) COMPLEXES

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It has been known for some time that aluminum(III) fails to form 3:1, 2:1, or even 1:1 complexes with 2-methyl-8-quinolinol in aqueous media. This has been attributed to the small ionic size of the aluminum ion and to steric interferences between the ligands in the 3:1 complex[1], and between the ligands and water molecules bound to the aluminum ion in the 2:1 and 1:1 complexes[2], as a result of the presence of the 2-methyl group on the chelating ligand. More recent work has shown that tris(2-methyl-8-quinolinolato)aluminum(III) can be precipitated from aqueous solution by very careful pH control[3]. Copper(II), on the other hand, has been observed to form 2:1 complexes with 2-methyl-8-quinolinol in 50% aqueous dioxane solutions[4–6], even though the planar orbitals of copper(II) might be expected to result in a maximum of steric interference between the ligands. This observation might be rationalized on the grounds of the slightly greater ionic radius of copper(II) and the strength of the soft acid–soft base interaction between copper(II) and the 2-methyl-8-quinolinolate anion. However, the stability constants for the formation of the 1:1 and 2:1 complexes of 2-methyl-8-quinolinol with copper(II) are smaller than the corresponding constants for 8-quinolinol with copper(II) in the same solvent[6,7], even though the Brønsted basicity of the 2-methyl derivative is slightly greater than that of 8-quinolinol. This suggests that the steric influences are indeed significant in the formation of the 2-methyl-8-quinolinolate copper(II) complexes.

Recently, a variety of substituted bis(8-quinolinolato) copper(II) chelates were studied for fungitoxic properties. Among these were the 7-halo, 2-methyl-7-halo, and 2-methyl-5-halo derivatives, all of which are potentially sterically hindered chelates. These groups of chelates demonstrated certain seemingly anomalous fungitoxic activities in their behavior compared with substituted bis(8-quinolinolato)copper(II) chelates which are not sterically hindered. In order to gain further insight into the physical nature and biological properties of these compounds, a study of their stability constants was undertaken. Because of solubility considerations and in order to simulate an aqueous environment, as nearly as possible, these studies were conducted in 75% (v/v) ethanol–water solutions.

EXPERIMENTAL

Reagent-grade copper(II) perchlorate (K and K Laboratories, Plainview, N.Y.)

was used without further purification. 2-Methyl-8-quinolinol (Aldrich Chemical Co., Milwaukee, Wisc.) was recrystallized from ethanol three times before use. Published methods were employed for the preparation of the remaining ligands as follows: 7-fluoro-8-quinolinol[8], 7-chloro-8-quinolinol[9], 7-bromo-8-quinolinol[9], 7-iodo-8-quinolinol[9,10], and the 5-fluoro-, 5-chloro-, 5-bromo-, 5-iodo-7-fluoro, 7-chloro-, 7-bromo-, and 7-iodo-2-methyl-8-quinolinols[11]. Potentiometric titrations and calibration of the glass electrode in 75% (v/v) ethanol–water mixture have been previously described[12]. The dissociation constants of the ligands and the stability constants of the 1:1 and 2:1 metal complexes were calculated from the potentiometric titration data on an IBM system 360 Model 65-digital computer with APL/360 language. Each constant was taken as the average of three titrations, each having a different ligand-to-metal ion formal concentration ratio. In no case was the average deviation more than 0.05 log unit.

RESULTS AND DISCUSSION

The dissociation constants of the ligands and their stability constants for formation of 1:1 (log k_1) and 2:1 (log k_2) complexes are presented in Table I. For purposes of comparison, the dissociation constants of 8-quinolinol[12], the 5-halo-8-quinolinols[13], and the corresponding stability constants with copper(II), determined in the same manner as the present results, are also included in Table I.

TABLE I

DISSOCIATION AND STABILITY CONSTANTS OF THE SUBSTITUTED 8-QUINOLINOLS AND THEIR COPPER(II) CHELATES

8-Quinolinol derivative	*Dissociation constants*		*Stability constants with copper(II)*	
	pKa_1	pKa_2	$\log k_1$	$\log k_2$
Unsubstituted[a]	4.33	11.30	11.95	11.01
5-Fluoro[b]	3.74	10.62	10.78	10.21
5-Chloro[b]	3.68	10.45	10.75	10.16
5-Bromo[b]	3.67	10.10	10.20	9.85
5-Iodo[b]	3.09	9.82	9.77	9.61
7-Fluoro	3.70	10.00	8.93	6.82
7-Chloro	3.07	9.59	8.11	6.33
7-Bromo	3.10	9.80	8.33	6.42
7-Iodo	3.02	10.70	8.39	7.27
2-Methyl	4.45	11.63	10.97	7.74
2-Methyl, 5-fluoro	3.84	11.47	10.38	7.87
2-Methyl, 5-chloro	3.68	10.68	9.45	7.09
2-Methyl, 5-bromo	3.70	10.78	9.08	7.51
2-Methyl, 5-iodo	3.23	10.05	8.83	6.91
2-Methyl, 7-fluoro	4.00	10.05	9.11	6.73
2-Methyl, 7-chloro	3.30	9.41	8.18	5.57
2-Methyl, 7-bromo	3.18	9.82	8.52	5.84
2-Methyl, 7-iodo	3.50	10.82	8.41	6.57

[a] Data from ref. 13.

[b] Data from ref. 12.

The pKa_1 values of the substituted 8-quinolinols correspond to dissociation from the protonated ring nitrogens. The pKa_2 values correspond to dissociation of the phenolic groups. With the exception of the iodo derivatives, the phenolic groups of the 7-halo derivatives are more acidic than those of the corresponding 5-halo compounds. Apparently, the proximity of the halogen atoms in the 7-halogeno derivatives to the phenolic groups allows the electron withdrawing effect of the halogen atoms to become the dominating factor in influencing the strengths of the O–H bonds.

Among the iodo derivatives, the 7-iodo substituent does not enhance the acidity of the phenolic group nearly as much as the 5-iodo substituent. This result implies that there is considerable charge transfer in the ground electronic state from the 7-iodo substituent to the phenolic group. With respect to dissociation of the protonated ring nitrogen atoms, the chloro and bromo substituents in the 7-position enhance acidity more than those in the 5-position, while the fluoro and iodo substituents in the 7-position are either slightly more acidity-enhancing or comparable in strength to the corresponding substituents in the 5-position. This suggests that the effect of halogen substitution on the dissociations of the protonated ring nitrogens is predominantly electronic in nature. The chlorine and bromine atoms act by accepting π-electrons from the aromatic system into vacant d orbitals, while the fluorine atom, having no low-lying vacant d orbitals, and the iodine atom, being highly polarizable, act as π-donors. The relative strengths of the electromeric effects in the 5- and 7-positions are probably governed by proximity considerations. The presence of the 2-methyl group in most cases appears to have a slight acidity weakening effect, as anticipated.

The successive formation constants for the 1:1 complexes (log k_1) and the 2:1 complexes (log k_2) of the 5-halogeno-8-quinolinols with copper(II) follow, approximately, the relative Brønsted basicities of the respective ligands. The log k_1 values of the 7-halogeno-8-quinolinols with copper(II) also follow this order, approximately, except that the fall in complex stability with decreasing basicity of the ligand is somewhat more dramatic than anticipated. This is also apparent in the log k_2 values. For the complexes of 2-methyl-8-quinolinol with copper(II), the stability constants are slightly lower than those of 8-quinolinol with copper(II) for the formation of the 1:1 chelate, and considerably lower for the formation of the 2:1 chelate from the 1:1 complex and ligand. This is in spite of the fact that the 2-methyl derivative is a slightly stronger Brønsted base than 8-quinolinol. Similarly, the 2-methyl derivatives of the 5-halogenated 8-quinolinols form weaker 1:1 and 2:1 complexes with copper(II) than their unmethylated counterparts.

The lower stabilities of 2-methyl-5-halogeno-8-quinolinol chelates with a variety of other transition metals relative to the corresponding unmethylated chelates have been observed in a recent study carried out in 75% (v/v) dioxane–water mixture[14]. In this study, the lower stability of the chelates of the 2-methyl-8-quinolinol derivatives was attributed to steric hindrance, resulting from the presence of the 2-methyl group. The results obtained here support this conclusion and also suggest that the hypothesis of steric hindrance be extended to the chelates of the 7-halo compounds. In this regard, it is extremely interesting that the log k_1 values of the 2-methyl-7-halo-8-quinolinol–copper(II) chelates are very close to those of the corresponding unmethylated chelates, while the log k_2 values of the 2-methyl-7-

halo derivatives are similar to, or only slightly lower than, those of the unmethylated derivatives. This indicates that the steric effects of the 2-methyl and 7-halo substituents are not additive, a result which is possible only if the chelates are not truly planar.

Such a conclusion can be rationalized as follows. The lower stabilities of the sterically hindered chelates, relative to the unhindered chelates, result from repulsions between the 2-methyl groups or 7-halo atoms and the solvent molecules coordinated through the dsp^2 orbitals of the copper(II) ion, in the case of the 1:1 chelates, and between the 2-methyl groups or 7-halo atoms of one ligand with the other coordinated ligand, in the case of the 2:1 chelates. If the hindered complexes were planar, introduction of a 2-methyl group into a coordinated 7-halo-8-quinolinolate ligand or of a 7-halo atom into a 2-methyl-8-quinolinolate ligand should result in additional repulsive destabilization energy. This was not observed. Alternatively, the repulsion between a 2-methyl group or a 7-halo atom and a coordinated solvent molecule or another ligand might result in the sterically hindered ligand twisting out of plane, to avoid already coordinated groups. In this case, the overlap between the donor orbitals of the hindered ligand and the square planar orbitals of the metal ion would be imperfect, resulting in a less stable complex than if maximal overlap with the planar orbitals of the metal ions occurred. The complex obtained would be intermediate in geometry between square planar and tetrahedral. Since the twisting out of plane would minimize repulsion between ligands, the introduction of an additional hindering group into the chelating ligand would be expected to have little effect upon the stability of the non-planar compound. This explanation is consistent with the experimental results obtained.

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SUMMARY

Stability constants of several bis(8-quinolinolato) copper(II) complexes substituted in the 7-, 2,7-, and 2,5-positions were determined by potentiometric titration in 75% (v/v) ethanol–water solution. The presence of a methyl group in the 2-position or halo atom in the 7-position causes steric hindrance between the ligands, resulting in non-planarity of the copper(II) complexes. This is evidenced by the non-additivity of the hindrance in the 2- and 7-positions.

RÉSUMÉ

On décrit une méthode de détermination de constantes de stabilité de plusieurs complexes cuivre(II)–bis(8-quinoléinol) substitués aux positions 7-, 2,7-, et 2,5-. On procède par titrage potentiométrique en milieu éthanol–eau 75% (v/v). On examine l'influence d'un groupe méthyl en position 2- et d'un atome d'halogène en position 7-.

ZUSAMMENFASSUNG

Die Stabilitätskonstanten von verschiedenen Bis-(8-Hydroxychinolinolato)–

Kupfer(II)-Komplexen, die in den 7-, 2,7- und 2,5-Stellungen substituiert sind, wurden durch potentiometrische Titration in 75 vol.-%iger äthanolisch–wässriger Lösung bestimmt. Das Vorliegen einer Methylgruppe in der 2-Stellung oder eines Halogenatoms in der 7-Stellung ruft eine sterische Hinderung zwischen den Liganden hervor, was zur nichtplanaren Struktur der Kupfer(II)-Komplexe führt. Dies wird dadurch belegt, dass die Hinderung in den 2- und 7-Stellungen nicht additiv ist.

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A NOVEL SYNTHESIS OF β-DIKETO DIESTERS AND THEIR ANALYTICAL POTENTIAL AS CHELATING AGENTS

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One of the most remarkable properties of the metal chelates of the β-diketones is their volatility. The fact that many of these chelates can be sublimed at low temperatures has led to their separation by gas chromatography[1] and fractional sublimation[2,3]. Many β-diketones have been synthesized with the idea of studying the volatile characteristics of their complexes[4-6], but any new β-diketone that would produce chelates of still greater volatility would have particular analytical importance.

It was envisioned that a macrocyclic ligand formed by joining both ends of two molecules of 2,4-pentanedione by straight-chain hydrocarbon groups might have interesting properties. Any metal ion chelated by such a ligand conceivably would be enclosed in a hydrocarbon-like shell which should enhance the volatility of the chelate. Furthermore, some selectivity might be introduced into the chelation reaction by varying the number of carbon atoms (ring size) in the macrocyclic ligand. Molecular models indicated that the minimum ring size would have to be approximately 22 carbon atoms to accommodate a central metal ion without strain.

Coombs and Houghton[7] have synthesized macrocyclic β-diketones, but they utilized aromatic groups as a means of constructing the ring. It was assumed that these aromatic macrocyclic chelates would not be particularly volatile for two reasons. First, it is known that chelates of aromatic 1,3-diketones, such as dibenzoylmethane, are not as volatile as the chelates of the aliphatic 1,3-diketones[1]. Secondly, the high molecular weight of these compounds would tend to decrease the volatility further. Therefore, non-aromatic macrocyclic β-diketones should offer a greater potential for increasing the volatility of chelates.

Thus, the present studies are directed to finding synthetic routes to C_{22}–C_{26} macrocyclics with emphasis on the inclusion of two symmetrically positioned β-diketone groups within the ring. This paper reports a novel synthesis for the preparation of β-diketone diesters and a number of new compounds that were synthesized as intermediates in route to the proposed macrocyclic compounds. The synthetic scheme proposed in this work has the advantage that the starting materials, which are the cyclonones, are readily available and relatively inexpensive. Gelin *et al.*[8] have reported the synthesis of β-diketone diesters by reacting a β-oxodiester with the appropriate acid chloride.

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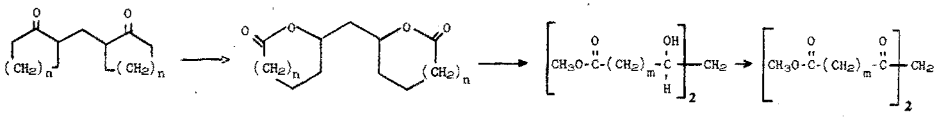
Bis(2-oxocyclopentyl)methane (I) and bis(2-oxocyclohexyl)methane (II) were prepared by a base-catalyzed condensation of the appropriate cyclonone with paraformaldehyde, as reported by Colonge *et al.*[9]. I and II were treated with 2 molar equivalents of perbenzoic acid in dichloromethane in the presence of sodium hydrogen carbonate, respectively, to give bis(3-oxo-2-oxacyclohexyl)methane (III) and bis-(3-oxo-2-oxacycloheptyl)methane (IV). Treatment of III and IV, respectively, with methanol and hydrochloric acid gave dimethyl-5,7-dihydroxyundecanedioate (V) and dimethyl-6,8-dihydroxytridecanedioate (VI). V and VI in acetone were oxidized by addition of chromic acid to give dimethyl-5,7-dioxoundecanedioate (VII) and dimethyl-6,8-dioxotridecanedioate (VIII), respectively. VII and VIII were isolated as their copper chelates. VIII was further characterized by forming the diacid derivative, 6,8-dioxotridecanedioic acid (IX). The synthetic scheme is outlined in Fig. 1.



I n=1
II n=2

III n=1
IV n=2

V m=3
VI m=4

VII m=3
VIII m=4

Fig. 1. Scheme of synthesis.

EXPERIMENTAL

Apparatus and reagents

When available, reagents and solvents were analytical reagent-grade materials that were used without further purification. Spectra utilized for the characterization of the new compounds were recorded on the Varian A-60A or the Varian HA-100 n.m.r. spectrometer, the Beckman IR-10, the Varian M-66 mass spectrometer and the Beckman DB spectrophotometer. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. The carbon–hydrogen analyses were performed by Mr. Ralph Seab, Coates Chemical Laboratories.

Synthetic procedure

Bis(3-oxo-2-oxacyclohexyl)methane (III). Procedures for the Baeyer-Villiger[10] reaction were followed in this synthesis. Bis(2-oxocyclopentyl)methane (18 g, 0.1 *M*) in 50 ml of dichloromethane was added dropwise to a cold stirred solution of 30.4 g (0.22 mole) of perbenzoic acid[11] and 10 g of anhydrous sodium hydrogencarbonate in 350 ml of dichloromethane. The reaction was stirred overnight at room temperature. The absence of the starting material was verified by thin-layer chromatography. (Silica gel was used as the adsorbent and ethyl acetate was used as the eluting solvent.) Anhydrous magnesium sulfate (5 g) were added, and the solution was filtered and concentrated.

A portion of the mixture (0.30 g) was chromatographed on a silica gel column by eluting with 500 ml of a 20% ethyl acetate–petroleum ether mixture. The first fraction contained 0.18 g of benzoic acid, and was followed by 0.11 g of the bis(3-oxo-2-oxacyclohexyl)methane. Recrystallization of the latter product from tetrachloromethane yielded 0.09 g of white solid, which melted at 95–97°.

Analytical data were as follows: i.r. max. (CH_2Cl_2) 1735, (CO) 1072, and

1050 cm^{-1}; n.m.r. ($CDCl_3$) 4.90–4.31 (m, methine H), 2.72–1.5 (m) p.p.m.; mass spectrum (70 eV) *m/e* (rel. intensity) 212 (0.7), 194 (15), 184 (16), 166 (9), 156 (37), 143 (29), 138 (11), 125 (22), 114 (55), 113 (13), 100 (19), 99 (100). Calculated for $C_{11}H_{16}O_4$, 62.25 % C, 7.6 % H; found, 62.2 % C, 7.6 % H.

Dimethyl 5,7-dihydroxyundecanedioate (*V*). The crude mixture from the preceding reaction containing the benzoic acid and bis(3-oxo-2-oxacyclohexyl)-methane was dissolved in 250 ml of anhydrous methanol. The solution was saturated with hydrogen chloride gas, refluxed for 12 h, cooled, and poured into 500 ml of saturated sodium chloride solution. The aqueous solution was extracted several times with 100-ml portions of dichloromethane. The combined organic extracts were washed with 50 ml of a 5% solution of sodium hydrogencarbonate, dried over magnesium sulfate and concentrated. After the mixture had been left under reduced pressure for 24 h at room temperature, a yellow solid residue remained. Recrystallization from an ether–petroleum ether mixture gave 12 g (43% yield) of white solid, which melted at 61–63°.

Analytical data were as follows: i.r. max. (KBr) 3525–3250 (OH), 2960, 2940, 2920, 1735 (CO), 1440, 1415, 1382, 1350, 1320, 1285, 1230, 1195, 1175, 1120, 1100, 1032, 980, and 835 cm^{-1}; n.m.r. ($CDCl_3$) 3.67 (s, CH_3OCO), 3.09 (b, OH) 4.1–3.7 (m), 2.5–2.1 (m), and 2.0–1.2 (m) p.p.m. Calculated for $C_{13}H_{24}O_6$, 56.5 % C, 8.75 % H; found, 56.45 % C, 8.6 % H.

Bis(3-oxo-2-oxacycloheptyl)methane (*IV*). A solution of 21 g (0.1 mole) of bis(2-oxocyclohexyl)methane (II) in 50 ml of dichloromethane was added to a cold, well-stirred solution of 30.4 g (0.22 mole) of perbenzoic acid[11] and 10 g of anhydrous sodium hydrogencarbonate in 350 ml of dichloromethane. The mixture was stirred overnight at room temperature, and 5 g of anhydrous magnesium sulfate were added. The mixture was filtered, concentrated and subjected to n.m.r. analysis: n.m.r. ($CDCl_3$) 4.8–4.2 (m, methine H), 2.8–2.2 (m), and 2.1–1.2 (m) p.p.m. The compound was not isolated but used directly in the next synthesis.

Dimethyl 6,8-dihydroxytridecanedioate (*VI*). The crude solid mixture from the previous reaction was dissolved in 300 ml of anhydrous methanol and was saturated with hydrogenchloride gas. After refluxing overnight, the mixture was poured into 500 ml of saturated sodium chloride solution and extracted 4 times with 100-ml portions of dichloromethane. The combined organic extracts were washed with 50 ml of 5% sodium hydrogencarbonate solution, dried over magnesium sulfate and concentrated. The resulting mixture was placed under reduced pressure overnight, and the product was recrystallized from an ether–petroleum ether mixture. A white solid (19.0 g, 63% yield), which melted at 61–62°, was collected.

Analytical data were as follows: i.r. max. (KBr) 3300 (OH), 2930, 1740 (CO), 1460, 1435, 1415, 1380, 1368, 1320, 1265, 1225, 1190, 1170, 1120, 1098, 1062, 1030, 980, and 870 cm^{-1}; n.m.r. ($CDCl_3$) 3.67 (s, CH_3O–CO), 3.1–2.8 (b-OH), 4.1–3.8 (m), 2.5–2.1 (m), and 1.8–1.3 (m) p.p.m. Calculated for $C_{15}H_{28}O_6$, 59.2 % C, 9.3 % H; found, 58.9 % C, 8.9 % H.

Dimethyl 5,7-dioxoundecanedioate (*VII*). The oxidation of β-diols has been reported by Kaye and Mathews[12]. A solution of 5.5 g (0.02 mole) of dimethyl-5,7-dihydroxyundecanedioate (V) in 100 ml of acetone was cooled to 0.5° in a 250-ml round bottom flask. The mixture was stirred and 22 ml of cold Jones reagent[13] (8 *M* chromic acid) were added dropwise while maintaining a temperature below

5°. The mixture was stirred for 1 h, and then 5 ml of isopropanol were added to decompose any excess of chromic acid. The mixture was poured over 500 g of crushed ice that contained 3 ml of concentrated sulfuric acid. The aqueous layer was extracted several times with dichloromethane and the combined organic extracts were washed with 100 ml of saturated sodium chloride solution, dried over magnesium sulfate and concentrated. The residue was dissolved in 50 ml of methanol and added to 5 g of copper acetate in 250 ml of water. The mixture was stirred overnight, and was extracted several times with dichloromethane. The combined organic extracts were dried and concentrated, affording 3.0 g of crude blue solid that was recrystallized from 95% ethanol. A blue precipitate was collected that did not sublime at reduced pressures but melted at 111–113°.

Analytical data were as follows: i.r. max. (KBr) 1735 (ester CO), 1575, 1520, 1450, 1370, 1350, 1215 and 1165 cm^{-1}; u.v. max. (C_2H_2OH) 296 nm (ε 22,000). Calculated for $CuC_{26}H_{38}O_{12}$, 51.5% C, 6.3% H; found, 51.7% C, 6.4% H.

The copper chelate of dimethyl-5,7-dioxoundecanedioate (1 g) was dissolved in 100 ml of 1 *M* hydrochloric acid and was extracted 4 times with 25-ml portions of dichloromethane. The organic extracts were washed with water, dried over magnesium sulfate and concentrated, giving 0.73 g of a clear liquid. The material crystallized upon standing in the refrigerator, but melted at room temperature.

Analytical data were as follows: i.r. max. (neat) 1735, 1710 (shoulder), 1615, 1440, 1370, and 1205 cm^{-1}; n.m.r. ($CDCl_3$) 5.55 (s, enol form), 3.67 (s, CH_3O–CO), 3.63 (s, keto) and 2.8–17 (m) p.p.m. Calculated for $C_{13}H_{20}O_6$, 57.3% C, 7.4% H; found, 57.45% C, 7.2% H.

Dimethyl 6,8-*dioxotridecanedioate* (*VIII*). A solution of 11.5 g (0.038 mole) of dimethyl-6,8-dihydroxytridecanedioate in 250 ml of acetone was cooled in an ice bath and Jones reagent[13] (8 *M* chromic acid) was added dropwise with constant stirring until the green color had changed to a dull brown color. The mixture was stirred for 10 min and then was poured into 200 ml of cold 1 *M* hydrochloric acid. The product was extracted several times into dichloromethane and the organic extracts were washed with 100 ml of saturated sodium chloride solution, dried over magnesium sulfate and concentrated. The residue was dissolved in 100 ml of ethanol and was added to a solution of 4 g of copper acetate in 100 ml of distilled water. The mixture was stirred for 1 h, then 100 ml of water were added and the mixture was filtered. The volume of mother liquid was reduced by one-half on the steam bath. The solution was cooled in an ice bath and the blue crystals were filtered. The combined solids were recrystallized from 95% ethanol, affording 3 g (30% yield) of blue needle crystals which did not sublime at reduced pressures but melted at 109–110°.

Analytical data were as follows: i.r. max. (KBr) 2950, 1735 (ester CO), 1565, 1518, 1455, 1440, 1420, 1378, 1310, 1260, 1238, 1218, 1202, 1180, 1160, 1125, 1075, 975, and 775 cm^{-1}; u.v. max. (C_2H_5OH) 296 nm (ε, 25,000). Calculated for $CuC_{30}H_{46}O_{12}$, 54.4% C, 7.0% H; found, 54.4% C, 7.0% H.

The copper chelate of dimethyl-6,8-dioxotridecanedioate (1.0 g) was dissolved in 50 ml of dichloromethane and extracted with 25 ml of 1 *M* hydrochloric acid. After the organic layer was dried and concentrated, 0.81 g of oily residue remained. The material crystallized on cooling and was recrystallized from an ether–petroleum ether mixture. The white solid melted at 30–31°.

Analytical data were: i.r. max. (KBr) 1740, 1710 (shoulder), 1615, 1440, 1370, and 1205 cm^{-1}; n.m.r. (CCl_4) 5.41 (s, enol), 3.46 (s, keto), 3.67 (s, CH_3O–CO), 2.4–2.1 (m), 1.8–1.4 (m) p.p.m. Calculated for $C_{15}H_{24}O_6$, 60.0% C, 8.05% H; found, 59.8% C, 8.0% H.

6,8-Dioxotridecanedioic acid. A solution of 0.41 g of dimethyl-6,8-dioxotridecanedioate in 5 ml of methanol was added to 25 ml of distilled water containing 2 ml of concentrated hydrochloric acid. The mixture was refluxed for 6 h and about one-half the solvent was evaporated on a rotary evaporator. The solution was placed in a refrigerator and 0.23 g of white crystalline material, which melted at 103–105°, was collected.

Analytical data were: i.r. max. (KBr) 3300–2500 (broad), 1700, 1610, 1460, 1440, 1408, 1320, 1260, 1205, 1130, 930, and 775 cm^{-1}; n.m.r. ($CDCl_3$) 9.0–8.0 (b, COOH), 5.51 (s, enol), 3.58 (s, keto), 2.7–2.1 (m) and 1.9–1.4 (m) p.p.m.; u.v. max. (C_2H_5OH) 276 nm (ε, 18,000). Calculated for $C_{13}H_{10}O_6$, 57.34% C, 7.40% H; found, 57.15% C, 7.40% H.

Copper salt of 6,8-dioxotridecanedioic acid. 6,8-Dioxotridecanedoic acid (100 mg) was added to 10 ml of a 5% solution of copper acetate. A blue precipitate was filtered, washed with ethanol and dried in the oven for 2 h at 90°. The compound melted at 250° with decomposition and was not soluble in the common organic solvents.

Analytical data: i.r. max. (KBr) 1610 (shoulder), 1560, 1515, and 1410 cm^{-1}. Calculated for $Cu_3C_{26}H_{34}O_{12} \cdot 2H_2O$, 40.8% C, 5.05% H, 24.9% Cu; found, 40.7% C, 5.4% H, 25% Cu.

DISCUSSION

This paper introduces a novel synthesis of symmetrical β-diketo diesters from readily available starting materials. Cyclopentanone and cyclohexanone, respectively, were condensed with paraformaldehyde in the presence of base to give I and II, as reported by Colonge *et al.*[9]. These workers reported a yield of 30% and 60%, respectively, but such yields were never realized in this work. Apparently, the reaction gives a variety of products and the yield of I and II varied from 1 to 15%. The crude separation of the desired compounds was achieved by distillation under reduced pressure and was accompanied by the codistillation of other products. Recrystallization was at times troublesome because of these extra components.

One major component that codistilled with I was identified as 2-cyclopentylidenecyclopentanone. The oily residue that remained after recrystallization of I was distilled under reduced pressure on a spinning band column, and the product was collected at 79–80° at 1 mm. 2-Cyclopentylidenecyclopentanone was identified by forming the oxime derivative that melted at 122–124° (lit. m.p. 123–124°)[14]. A satisfactory carbon–hydrogen analysis was obtained.

It is interesting to note that I was isolated in two crystalline forms, one melted at 68–70° (lit. m.p. 70°) and the other at 38° (lit. m.p. 38°), as reported by Colonge *et al.*[9]. Only a single constant melting isomer (60°) of II was isolated. The stereochemistry of I and II was determined by n.m.r. analysis of stereospecifically prepared disubstituted 2,2-dimethyldioxones[15]. The *dl* configuration was assigned to the 71° melting isomer of I and the 60° melting isomer of II.

I and II were treated with perbenzoic acid[14] in dichloromethane in the presence of sodium hydrogen carbonate, respectively, to give III and IV (90% yield). Attempts to extract the lactone (III) from the benzoic acid with a hydrogencarbonate solution resulted in the partial hydrolysis of III. III was isolated in sufficient quantity for characterization by column chromatography, but this method was impractical for preparative purposes, owing to the large amounts of benzoic acid that were formed.

III has not been reported previously. The n.m.r. spectrum contained a multiplet from 4.90 to 4.31 p.p.m. (2H). This multiplet was assigned to the methine proton and is consistent with that reported in the literature for $C–\underline{CH}–O–CO–R$ (4.8 p.p.m.)[16]. The i.r. spectrum showed a carbonyl absorption at 1735 cm^{-1} (6-membered lactone). The mass spectrum had a parent peak at 212 (mol. wt. 212.25). IV has previously been reported[17] and was not isolated.

V and VI were prepared by refluxing the crude mixture of benzoic acid and III and IV, respectively, with methanol and hydrogen chloride. Attempts to separate the methyl benzoate from V by distillation under reduced pressure failed, because V gave off methanol and reverted back to the lactone structure. The methyl benzoate was evaporated under reduced pressure at room temperature. Recrystallization of V and VI from an ether–petroleum ether mixture gave 43% and 63% yields, respectively.

V and VI were characterized by their n.m.r. spectra, each of which gave a singlet at 3.67 p.p.m. ($C\underline{H}_3O–CO$), a multiplet from 4.1 to 3.8 p.p.m. ($C\underline{H}–OH$), and a broad absorption from 3.1 to 2.8 p.p.m. (OH), that disappeared upon the addition of D_2O. The i.r. spectra each showed an OH stretch at 3300 cm^{-1} and ester carbonyl absorption at 1740 cm^{-1}.

V and VI in acetone were oxidized by addition of chromic acid to give VII and VIII which were isolated as their copper chelates (20% and 30% yield, respectively). The copper chelate of VII gave i.r. absorptions at 1575 ($C\!=\!C$), 1520 ($C\!=\!O$) and 1735 (ester CO) cm^{-1}. The copper chelate of VIII gave i.r. absorptions at 1570 ($C\!=\!C$), 1520 ($C\!=\!O$) and 1735 (ester CO). The u.v. maximum for both compounds occurred at 296 nm (298 nm for copper acetylacetonate). Attempts to sublime the copper chelates under reduced pressure resulted in the decomposition of the complexes around 200° at 1 mm pressure.

VII and VIII were isolated by destroying their copper chelates with acid. The n.m.r. spectrum of VII had singlets at 5.55 p.p.m. (enol form), 3.63 p.p.m. (keto form), and 3.67 p.p.m. ($C\underline{H}_3O–CO$). The n.m.r. spectrum of VIII had singlets at 5.41 p.p.m. (enol form), 3.46 p.p.m. (keto form), and 3.67 p.p.m. ($C\underline{H}_3O–CO$). Their i.r. spectra gave the characteristic 1735 cm^{-1} ester carbonyl absorptions and the characteristic absorption at 1610 cm^{-1} (β-diketones).

VIII was further characterized by forming the diacid derivative, 6,8-dioxotridecanedioic acid (IX). The n.m.r. spectrum of IX showed absorptions from 9.0 to 8.0 p.p.m. (b, $COO\underline{H}$), 5.52 p.p.m. (s, enol form), 3.58 p.p.m. (s, keto form). The i.r. spectrum gave absorptions at 3000 cm^{-1} (COOH), 1100 cm^{-1} ($C\!=\!O$), and 1610 cm^{-1} ($C\!=\!C$).

6,8-Dioxotridecanedioic acid (IX) was added to a solution of copper acetate and a blue solid was formed. The possible structures for this complex are intriguing and are projected in Fig. 2. The i.r. spectrum gave absorptions at 1610 cm^{-1} (shoulder), which is assigned to the CO antisymmetric stretch of the carboxylate anion[18],

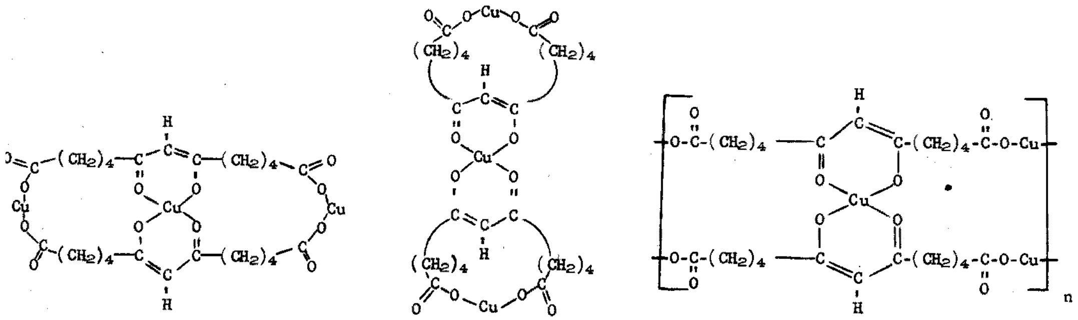


Fig. 2. Possible structures of copper salt of 6,8-dioxotridecanedioic acid.

absorptions at 1570 and 1520 cm^{-1} (chelated diketone) and a strong absorption at 1400 cm^{-1} (symmetric stretch of the carboxylate anion[18]. The complex was insoluble in all the common organic solvents and decomposed at 250° with no evidence of subliming. The elemental analysis indicated two waters of hydration.

Chelating properties of the new compounds

The chelating ability of VII, VIII, and IX with a number of common metal ions was determined and the results are summarized in Table I. The general procedure for forming the chelates was as follows: five drops of 10% β-diketone in ethanol were added to 5 drops of 10% metal salt solution, which was buffered with 3–5 drops of 10% sodium acetate. The solution was allowed to stand for 2 h. For those in which no reaction was observed, the aqueous solution was extracted with 10 drops

TABLE I

CHELATION SURVEY FOR THE β-DIKETONES

Metal ion	*Dimethyl-5,7-dioxo-undecanedioate*	*Dimethyl-6,8-dioxo-tridecanedioate*	*6,8-Dioxotridecane-dioic acid*
Be(II)	White ppt.	White ppt.	White ppt.
Ca(II)	NR[a]	NR[a]	NR[a]
Cd(II)	NR	NR	NR
Co(II)	Pink ppt.[b]	Pink ppt.[b]	NR
Cr(III)	NR	NR	NR
Cu(II)	Blue ppt.	Blue ppt.	Blue ppt.
Fe(III)	Red color	Red color	Red color
La(II)	NR	NR	White ppt.
Mg(II)	NR	NR	NR
Mn(II)	NR	NR	NR
Ni(II)	Green ppt.[b]	Green ppt.[b]	NR
Pd(II)	Yellow ppt.	Yellow ppt.	Yellow ppt.
Pt(II)	NR	NR	NR
UO(II)	NR	NR	Yellow ppt.
Zn(II)	NR	NR	NR

[a] No observed reaction.

[b] Colored product observed only after extracting with CH_2Cl_2 and evaporating.

of dichloromethane and the organic layer was evaporated to dryness to detect any extracted components as a residue.

Beryllium(II), copper(II) and palladium(II) immediately formed complexes (precipitates) with these ligands. Iron(III) formed the characteristic red color of the enolic complexes, and the uranyl ion formed a yellow precipitate with IX. The cobalt(II) and nickel(II) complexes of VII and VIII were isolated after extracting the aqueous solution with dichloromethane. Under the same conditions, 2,4-pentanedione formed precipitates with all these metals. Thus, the β-diketo diesters appear to be much more selective than 2,4-pentanedione and they might offer some analytical application in the areas of extraction and gravimetry.

It is not surprising that these new chelates were not volatile at reduced pressures over the temperature range of 100–250°, as are so many of the other β-diketone chelates. The very polar terminal ester groups of the chelates must lead to high intermolecular attractions which greatly reduce or inhibit the volatility.

This work was supported in part by a National Science Foundation Science Faculty Fellowship (C.J.A.).

SUMMARY

A novel procedure has been developed for the synthesis of dimethyl-5,7-dioxoundecanedioate, dimethyl-6,8-dioxotridecanedioate and 6,8-dioxotridecanedioic acid from readily available starting materials. The various intermediate and final products of the synthesis were characterized by chemical analyses and by n.m.r., i.r. and mass spectrometry. The chelating ability of the new β-diketones was compared with that of acetylacetone (2,4-pentanedione) on fifteen common metal ions. The β-diketo diesters readily formed precipitates with Be(II), Cu(II) and Pd(II) and red complexes with Fe(III). The green Ni(II) and pink Co(II) complexes were observed only after extracting the aqueous solution with dichloromethane. The β-diketo diacid reacted readily only with Be(II), Cu(II), Pd(II) and UO(II) to form precipitates.

Under the same conditions 2,4-pentanedione formed precipitates with all of the ions surveyed. The copper(II) chelates of the two β-diketo diesters were characterized completely. They were stable, soluble in dichloromethane, toluene and xylene, but did not sublime at elevated temperatures and reduced pressures. The copper(II) chelate of 6,8-dioxotridecanedioic acid was characterized and three possible structures are proposed for the complex which exhibits a ligand: metal ratio of 2:3.

RÉSUMÉ

Un nouveau procédé est mis au point pour la synthèse du diméthyl-5,7-dioxoundécanedioate, du diméthyl-6,8-dioxotridécanedioate et de l'acide 6,8-dioxotridécanedioïque. Les divers produits intermédiaires et finals de la synthèse sont caractérisés par analyse chimique et spectrométrie n.m.r., i.r. et de masse. L'aptitude de ces nouvelles β-dicétones à former des chélates est comparée à celle de l'acétylacétone, avec quinze ions métalliques courants. On examine spécialement les chélates obtenus avec le cuivre(II).

ZUSAMMENFASSUNG

Es wurde ein neues Verfahren zur Darstellung von Dimethyl-5,7-dioxoundecandiat, Dimethyl-6,8-dioxotridecandiat und 6,8-Dioxotridecandisäure unter Verwendung leicht erhältlicher Ausgangssubstanzen entwickelt. Die verschiedenen Zwischen- und Endprodukte der Synthese wurden durch chemische Analysen und durch n.m.r.-, i.r.- und Massenspektrometrie charakterisiert. Die Chelatisierungsfähigkeit der neuen β-Diketone wurde bei fünfzehn üblichen Metallionen mit derjenigen von Acetylaceton (2,4-Pentandion) verglichen. Die β-Diketodiester bildeten leicht Niederschläge mit Be(II), Cu(II) und Pd(II) und rote Komplexe mit Fe(III). Die grünen Ni(II)- und blassroten Co(II)-Komplexe wurden nur nach Extraktion der wässrigen Lösung mit Dichlormethan beobachtet. Die β-Diketodisäure reagierte leicht nur mit Be(II), Cu(II), Pd(II) und UO(II) unter Bildung von Niederschlägen. Unter denselben Bedingungen bildete 2,4-Pentandion Niederschläge mit allen untersuchten Ionen. Die Kupfer(II)-Chelate der beiden β-Diketodiester wurden vollständig charakterisiert. Sie waren beständig, lösten sich in Dichlormethan, Toluol und Xylol, sublimierten aber nicht bei erhöhten Temperaturen und verminderten Drucken. Das Kupfer(II)-Chelat von 6,8-Dioxotridecandisäure wurde charakterisiert, und es werden für den Komplex, der ein Ligand: Metall-Verhältnis von 2:3 hat, drei mögliche Strukturen vorgeschlagen.

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IONIZATION EQUILIBRIA AND ELECTRONIC SPECTROSCOPY OF THE CHELATING QUINOLINECARBOXYLIC ACIDS

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Quinoline-2-carboxylic acid (quinaldic acid) and quinoline-8-carboxylic acid have considerable importance in analytical chemistry as chelating agents and have been employed for the determination of several metal ions[1–3]. The dissociation constants of these ligands have been determined potentiometrically by several workers[1,3,4]. While these results are in good agreement, the assignments of the dissociation constants to the proper equilibria appear to be controversial. Elderfield and Siegel[4] have made correlations of the dissociation constants of all of the isomeric quinolinecarboxylic acids with the rates of hydrolysis of their methyl esters and concluded that the prototropic equilibria occurring in the middle of the pH region involved protonation of the anion at the carboxylate group. However, Holmes and Crimmin[1] and Lumme[3] have argued that the equilibria occurring in the middle pH region entail protonation at the heterocyclic nitrogens of the anion while the equilibria occurring in acidic media (*ca.* pH 2) involve protonation of the zwitterion at the carboxylate groups to form the singly charged cations[1,2]. Electronic absorption spectroscopy affords a satisfactory conclusion to this controversy because the changes produced in the absorption spectrum by protonation of a heterocyclic nitrogen atom are generally different from those produced by protonation of an aromatic carboxylate anion. In addition, we are interested in the fluorescence spectroscopies of these compounds because of the potential utility of these methods for ultrasensitive analysis of the ligands and of their metal complexes and also because of the information of photochemical significance which may be derived from fluorescence spectra. Consequently, it was decided to undertake the present study of the acidity dependences of the electronic absorption and fluorescence spectra of quinaldic acid, quinoline-8-carboxylic acid and their methyl esters.

EXPERIMENTAL

Reagents

Quinaldic acid (Aldrich Chemical Co., Inc., Milwaukee, Wisc.) and quinoline-8-carboxylic acid (Pfaltz and Bauer, Inc., Flushing, N.Y.) were recrystallized from 50% aqueous ethanol. The methyl esters were prepared by the procedure of Elderfield and Siegel[4].

Solutions employed to study the Hammett acidity range were prepared by dilution of analytical reagent-grade sulfuric acid (Mallinckrodt) with distilled deionized water. The corrected Hammett acidity scale[5] was employed to calibrate the sulfuric acid solutions. Citrate and phosphate buffers as well as sodium hydroxide solutions in distilled, deionized water were used to study the pH range.

A 100-μl micropipet was used to deliver the stock solutions of quinaldic acid and quinoline-8-carboxylic acid to 10-ml volumetric flasks, containing the appropriate acid or buffer solutions, immediately before the taking of spectra, in order to minimize decomposition errors.

Apparatus

pH measurements were made on an Orion model 801 digital pH meter with a Beckman combination glass–silver–silver chloride electrode. Absorption spectra were recorded on a Beckman DB-GT spectrophotometer. Fluorescence spectra were taken on a Perkin-Elmer MPF-2A fluorescence spectrophotometer whose monochromators were calibrated against the xenon line emission spectrum and whose output was corrected for instrumental response by means of a rhodamine-B quantum counter.

RESULTS

Absorption spectra

The pertinent spectral features of the electronic absorption spectra of quinaldic acid, quinoline-8-carboxylic acid and their methyl esters, are presented in Tables I and II. The absorption spectra of quinoline-8-carboxylic acid (Fig. 1) and its methyl ester in alkaline and acid media, respectively, are remarkably like those of quinoline

TABLE I

ELECTRONIC ABSORPTION AND FLUORESCENCE SPECTRAL FEATURES OF QUINALDIC ACID AND ITS METHYL ESTER AT VARIOUS ACIDITIES

(The concentrations of quinaldic acid and its methyl ester, in emission measurements, were $2.00\cdot10^{-5}$ *M* and $1.00\cdot10^{-5}$ *M*, respectively. For absorption measurements, the concentrations were ten times greater. Spectral maxima are reported in $\mathrm{cm}^{-1}\cdot10^{-4}$ ($\bar{\nu}$))

	Absorption				*Fluorescence* $\bar{\nu}$ *(max)*
	$\bar{\nu}(^1L_a)$	*log* $\varepsilon(^1L_a)$	$\bar{\nu}(^1L_b)$	*log* $\varepsilon(^1L_b)$	
Quinaldic acid					
pH 10.0	3.77	3.98	3.28	3.70	2.78
pH 3.0	—[a]	—[a]	3.12	4.02	2.46
pH 0.1	2.94sh[b]	3.60	3.12	3.98	—[c]
$H_0 -4.7$	2.94sh[b]	3.60	3.10	3.98	2.13
$H_0 -10.0$	2.94sh[b]	3.60	3.10	3.98	2.00
Methyl quinaldate					
pH 7.0	3.77	3.90	3.31	3.70	2.53
pH 0.1	3.00sh[b]	3.50	3.10	3.89	—[c]
$H_0 -5.8$	3.00sh[b]	3.50	3.10	3.89	2.18
$H_0 -10.0$	3.00sh[b]	3.50	3.10	3.89	1.98

[a] The ^1L_a band has red-shifted and is degenerate with the ^1L_b band.

[b] The ^1L_a band emerges as an unstructured shoulder on the long wavelength side of the ^1L_b band.

[c] No fluorescence is observed at pH 0.1.

TABLE II

ELECTRONIC ABSORPTION AND FLUORESCENCE SPECTRAL FEATURES OF QUINOLINE-8-CARBOXYLIC ACID AND ITS METHYL ESTER AT VARIOUS ACIDITIES

(The concentrations of quinoline-8-carboxylic acid and its methyl ester, in emission measurements, were $1.67 \cdot 10^{-5}$ *M* and $1.00 \cdot 10^{-5}$ *M* and $1.00 \cdot 10^{-5}$ *M*, respectively. For absorption measurements, the concentrations were ten times greater. Spectral maxima are reported in $\mathrm{cm}^{-1} \cdot 10^{-4}$ ($\bar{\nu}$))

	Absorption				*Fluorescence* $\bar{\nu}(max)$
	$\bar{\nu}(^1L_a)$	$\log \varepsilon(^1L_a)$	$\bar{\nu}(^1L_b)$	$\log \varepsilon(^1L_b)$	
Quinoline-8-carboxylic acid					
pH 10.0	3.50	3.83	3.17	3.49	2.44
pH 4.0	—[a]	—[a]	3.15	3.89	2.47
pH 0.1	—[a]	—[a]	3.15	3.85	—[b]
$H_0 - 5.8$	—[a]	—[a]	3.15	4.02	2.60
$H_0 - 10.0$	—[a]	—[a]	3.15	4.03	2.60
Methyl quinoline-8-carboxylate					
pH 7.0	3.50	3.99	3.17	3.23	2.26
pH 0.1	—[a]	—[a]	3.15	3.85	—[b]
$H_0 - 5.8$	—[a]	—[a]	3.16	3.85	2.53
$H_0 - 10.0$	—[a]	—[a]	3.16	3.85	2.53

[a] The ^1L_a band has red-shifted and is degenerate with the ^1L_b band.
[b] No fluorescence is observed at pH 0.1.

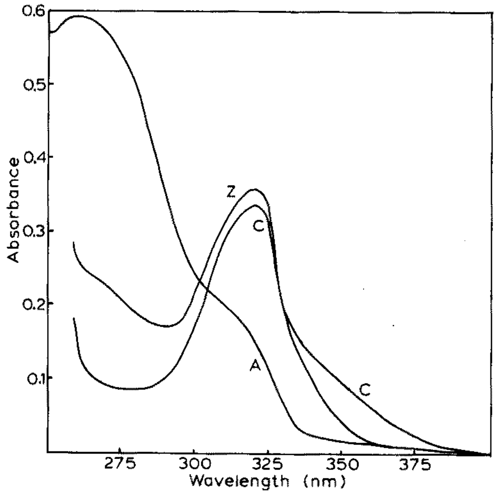


Fig. 1. Absorption spectra of quinaldic acid: (A) at pH 10.0, (Z) at pH 3.0, (C) at pH 0.

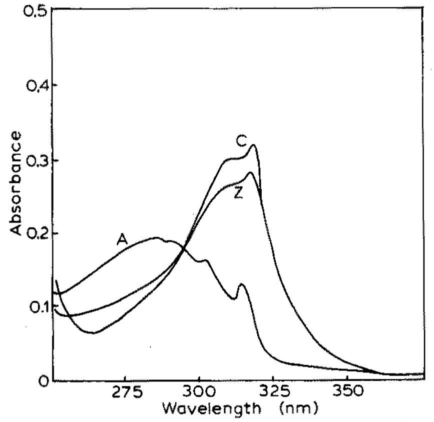


Fig. 2. Absorption spectra of quinoline-8-carboxylic acid: (A) at pH 10.0, (Z) at pH 4.0, (C) at pH 0.

and the quinolinium cation[6,7] in band forms and in vibrational structure. The absorption spectra of quinaldic acid (Fig. 2) and its methyl ester in alkaline and acid solutions, respectively, are similar to those of quinoline and the quinolinium ion in general appearance but the vibrational structure in all species derived from quinaldic acid is absent.

The pH dependences of the absorption spectra show that on going from alkaline to dilute acid solutions, a single proton is added, in the ground state, to the quinolinecarboxylate anions and to the neutral methyl esters. It is in this protonation step in all cases that the absorption spectrum changes from quinoline-like to quinolinium-like. Further increase in acidity produces in the compounds derived from the 8-isomer, barely perceptible changes, and in the compounds derived from the 2-isomer a long wavelength shoulder in the absorption spectra. The pK_a values obtained from the absorptiometric titrations are presented in Table III. In the cases of quinaldic acid and quinoline-8-carboxylic acid, the pK_a values obtained by absorptiometry are in agreement with those obtained potentiometrically[1,2]

TABLE III

PROTOTROPIC DISSOCIATION CONSTANTS OF QUINALDIC ACID, QUINOLINE-8-CARBOXYLIC ACID AND THEIR METHYL ESTERS FOR EQUILIBRIA OCCURRING IN THE ACIDITY RANGE pH 1.0 TO H_0 −10.0

(pK_{ZA} and pK_{CZ} correspond to the equilibria between the zwitterions derived from the free acids and the respective anions and cations. pK_{CN} corresponds to the cation–neutral species equilibria of the methyl esters. pK^*_{DC} corresponds to the doubly protonated–singly protonated cation equilibria in the excited state.)

	pK_{ZA}	pK_{CZ}	pK_{CN}	pK^*_{DC}
Quinaldic acid	4.9	1.6		−6.4
Quinaldic acid methyl ester			1.9	−7.0
Quinoline-8-carboxylic acid	6.9	2.2		−3.5
Quinoline-8-carboxylic acid methyl ester			5.0	−2.8

Fluorescence spectra

All fluorescences observed from the quinolinecarboxylic acids and their methyl esters were unstructured. The fluorescence maxima in pH and Hammett acidity regions representative of the species from which the emissions originated are shown in Tables I and II.

The extremely weak ultraviolet fluorescence of the 2-carboxylate anion is converted to the weak blue emission of the uncharged species in the pH range 7–3, the same pH interval in which the absorptiometric titration occurs. Similarly, the fluorimetric titrations of the anion-uncharged species interconversion of the 8-carboxylic acid and of the neutral-cation equilibria of both esters, occur in the same pH intervals in which the absorptiometric titrations were observed, indicating that the excited state prototropic processes are too slow to compete with fluorescence for deactivation of the excited state.

In the pH range 5–0 both carboxylic acids and both esters demonstrate variations in fluorescence properties with pH. In this range the fluorescence of the uncharged species derived from the 8-carboxylic acid is quenched with decreasing pH but no obvious changes in the absorption spectra occur. Similarly, the fluorescence of the neutral methyl-2-quinolinecarboxylate is quenched but the quenching occurs with the same titration characteristics observed for the absorption spectra. Similarly, changes in the fluorescence spectra occur in the 2-carboxylic acid and its methyl ester, which are accompanied by only subtle changes in the absorption spectra (Tables I and II).

In the Hammett acidity region, the fluorimetric titration behaviors of the 2-isomer and its methyl ester are similar (Fig. 3), showing initially an increase in fluorescence yield with increasing acidity and then a decrease in emission with further increase in acidity. In contrast, the fluorescences of the 8-isomer and its methyl ester rise to maximal values at low acidities and remain constant throughout the rest of the accessible Hammett acidity range. No discernible changes in absorption spectra accompany these fluorescence changes. It should be mentioned that the emission intensities of both isomers are much greater in concentrated acid than in aqueous media.

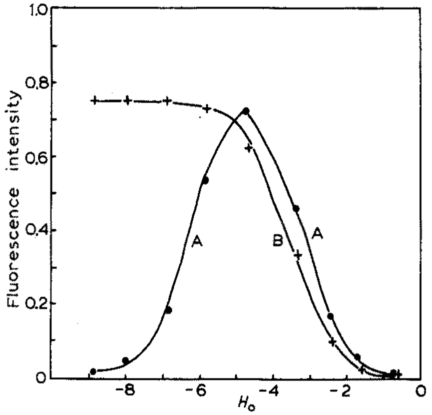


Fig. 3. Fluorimetric titrations of quinaldic acid and quinoline-8-carboxylic acid in aqueous–sulfuric acid media. (A) Variation of the relative quantum yield of the 470-nm fluorescence of quinaldic acid. (B) Variation of the 395-nm fluorescence of quinoline-8-carboxylic acid with Hammett acidity (H_0).

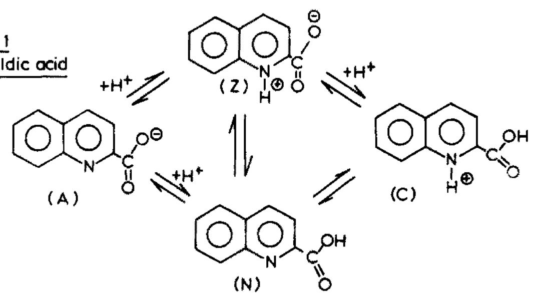
DISCUSSION

Absorption spectra and ground state ionization equilibria

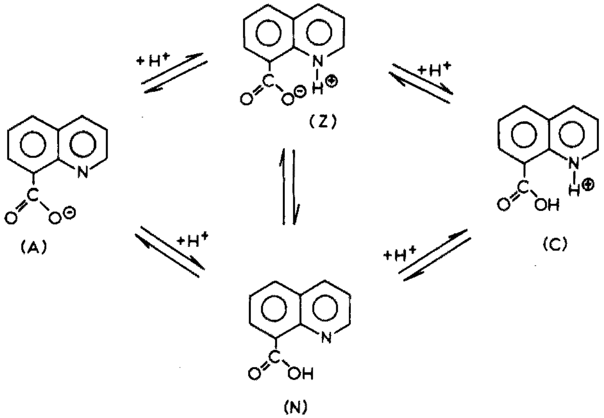
The possible ground state prototropic equilibria that can occur in quinaldic acid and quinoline-8-carboxylic acid in the pH region are represented in Scheme 1. That the equilibria observed absorptiometrically and potentiometrically in near neutral solutions are the same is supported by the excellent agreement between the spectrophotometrically determined constants and those determined by the electrometric procedure[1,2]. These equilibria occur between the anionic species (A) and the zwitterionic species (Z) rather than between the anions and the neutral species (N). This conclusion is supported by two experimental observations. First, the conversions of the quinoline-like absorption spectra of the anionic species in alkaline solutions to the quinolinium-like absorption spectra of the uncharged species strongly suggest that protonation occurs at the heterocyclic nitrogen atoms. Moreover, that these

Scheme 1

(a) Quinaldic acid



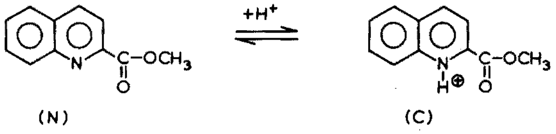
(b) Quinoline-8-carboxylic acid



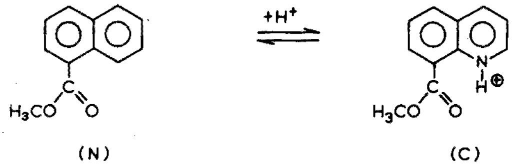
spectra are so similar to those of unsubstituted quinoline and the quinolinium ion indicates that in the ground states of the anions and uncharged species, the carboxylate groups are not conjugated with the aromatic rings and probably are planar with respect to the rings, affecting the electronic distributions in the aromatic systems only by rather small electrostatic polarizing effects. The protonations of the carboxylate groups of the 1- and 2-naphthoic acids, from which the quinolinecarboxylates may be thought to be derived, produce substantial red-shifting of the ^1L_a and ^1L_b bands, respectively[8], as the carboxyl groups are conjugated with the naphthalene rings and mix charge transfer character into the excited states of naphthalene with which they interact. The prototropic equilibria of the methyl esters of the quinolinecarboxylic acids may be represented as in Scheme 2. The neutral esters (N) may be thought of as models of the neutral species of the quinolinecarboxylic acids in which the carboxyl groups are constrained to remain undissociated. Protonation of the neutral esters in the pH range must occur at the ring nitrogen atoms since the carbomethoxy groups are not sufficiently basic in the ground state to become protonated at these acidities. The neutral esters show absorption spectra which are quinoline like in appearance, indicating that the carbomethoxy groups are not conjugated with the aromatic rings in the ground and Franck–Condon excited states. Protonation at the ring nitrogen atoms results in a quinolinium-like spectrum in the case of the

Scheme 2

(a) Methyl quinaldate



(b) Methyl quinoline-8-carboxylate



8-isomer and a near quinolinium-like spectrum in the case of the 2-isomer. The 2-isomer, on protonation, also develops a shoulder on the long wavelength side of the principal quinolinium absorption band very similar in appearance to that observed in acridine and in the 8-methylquinolinium ion[7]. These observations indicate that in the protonated esters which are very much like the singly protonated acids there is some degree of conjugation between the 2- carbomethoxy group and the quinolinium ring but not between the 8-carbomethoxy group and the quinolinium ring in the ground and Franck–Condon excited states. The conversions of the quinoline-like absorption spectra of the neutral esters to the quinolinium-like absorption spectra of the protonated esters (which are known to be protonated at the ring nitrogen atoms) with pK_a values different from those of the free acids confirm the assignment of the equilibria occurring in the free acids, in near neutral solutions, to the anionic and zwitterionic species.

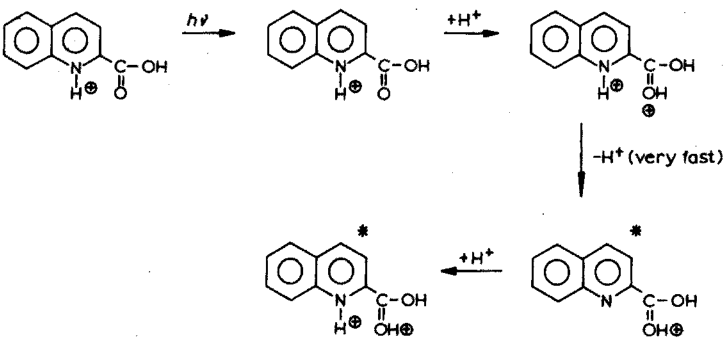
Lowering of the pH of solutions containing the zwitterionic species of the quinolinecarboxylic acids to the region near pH 2 has been shown, potentiometrically, to produce a second protonation, presumably at the carboxylate group[1,2]. In the case of the 2-isomer this transformation can be observed through the appearance of a long wavelength shoulder in the quinolinium-like spectrum, similar to that in the protonated ester, with decreasing pH. However, in the 8-isomer no such transformation is clearly discernible. Presumably, this is the result of failure of the carboxyl group of the 8-isomer to conjugate with the aromatic system so that the electrical perturbation produced by protonation of the carboxyl group barely affects the electronic structure of the aromatic ring and is thus not reflected in the near ultraviolet absorption spectrum. This represents a limitation to the utility of electronic absorption spectroscopy in the study of chemical phenomena which do not appreciably affect the energies of the optical electrons of reactive molecules. In concentrated sulfuric acid solutions no appreciable changes of the quinolinium-like absorption spectra of the protonated quinolinecarboxylic acids or their methyl esters, were observed. Arylcarboxylic acids derived from hydrocarbons are normally protonated at $H_0 \sim -9$[9], resulting in substantial red shifts of the absorption spectra. However, the positive charge residing in the quinolinium ring is probably delocalized, to some extent, onto the carboxyl and carbomethoxy groups of the quinolinecarboxylic acids and esters, respectively, resulting in lower basicity of the carboxyl and carbomethoxy groups. This effect could easily put the pK_a for protonation of these groups, in the ground state, out of reach of the most concentrated sulfuric acid solutions available in this study ($H_0-10.0$). Thus it is concluded that in the entire range of concentrated sulfuric acid solutions studied, the free acids and esters are exclusively in the singly charged cation form (C).

Fluorescence spectra

The fluorescence spectrum of the anion derived from quinaldic acid is similar to that of the 2-naphthoate anion ($\bar{\nu}_f = 2.81 \cdot 10^4$ cm^{-1} [8]), and lies at substantially lower frequencies than that of quinoline in water[6,7]. This suggests that in the lowest excited singlet state, the carboxylate group, subsequent to excitation, has rotated into coplanarity with the quinoline ring and emission occurs from a thermally equilibrated excited species in which the carboxylate group is conjugated with the aromatic system. Titration of the 2-quinaldate fluorescence with H^+ converts the fluorescence to that of the uncharged species. This titration occurs with the same characteristics as the corresponding absorptiometric titration and the emission of the resulting uncharged species is similar in frequency to that of the quinolinium ion[6,7] and considerably lower in frequency than that of 2-naphthoic acid ($\bar{\nu}_f = 2.63 \cdot 10^4$ cm^{-1} [8]). Thus it is concluded that the interconversion of the fluorescence in the near neutral pH region is static and involves the zwitterion as the excited uncharged species. This is probably a result of the diffusion-limited nature of the excited state prototropic exchange and the low concentration of H^+ in the middle pH region. In dilute acid solutions, the fluorescence of the zwitterion is quenched, half-quenching occurring at pH 1.6. In alkaline solutions, the neutral methyl ester of quinaldic acid fluoresces at frequencies much closer to those of 2-naphthoic acid than to those of quinoline. The fluorescence of the ester relative to that of the quinaldate anion indicates the conjugation of the carboxyl group with the aromatic ring in the excited state. Decreasing pH quenches the fluorescence of the methyl ester of quinaldic acid, with the same titration characteristics observed absorptiometrically. These results indicate that in the electronic configuration corresponding to the singly protonated cation, quinaldic acid is not fluorescent. The quenching of the fluorescence of the zwitterion occurs simultaneously with the appearance of the long wavelength shoulder in the absorption spectrum at low pH. Thus the quenching of the fluorescence of the zwitterion can be assigned to the ground state (static) conversion of the zwitterion to the singly protonated species derived from quinaldic acid.

In sulfuric acid media the fluorescence behavior of quinaldic acid is complex (Fig. 3). At H_0-1 a blue green fluorescence at $2.13 \cdot 10^4$ cm^{-1} appears, rises sigmoidally to a maximum at H_0-5 and then decreases sigmoidally, shifting to a weak emission at $2.00 \cdot 10^4$ cm^{-1} at H_0-10. This behavior suggests that two prototropic processes are occurring in the range H_0-1 to H_0-10. Because the singly charged cation is the only ground state species present throughout this region of acidity, the acidity dependence of the fluorescence of quinaldic acid in sulfuric acid must be the result of prototropic processes in the lowest excited singlet state. A similar dependence on Hammett acidity is observed for the methyl ester of quinaldic acid. Because the carbonyl type oxygen atoms are the only basic sites in singly protonated quinaldic acid and its methyl ester, the occurrence of two fluorimetric titration phenomena in these molecules is somewhat perplexing. It was considered that one protonation might occur at the carboxyl (or carbomethoxy) group and the other at carbon in the aromatic ring. However, protonation in the aromatic ring would remove a pair of electrons from the π-system and should either quench or drastically blue shift the fluorescence. Thus protonation in the aromatic ring does not seem likely. A plausible explanation for the fluorimetric titration behavior of quinaldic acid and its methyl ester can be advanced on the basis of one of the titration phenomena being due to phototautomerism in the lowest excited singlet state. Let us assume that in the lowest excited singlet state the carboxyl (or carbomethoxy) group is more basic than the ring nitrogen atom. In sulfuric acid solutions weaker than H_0-1, the excited singly charged cation, protonated at the ring nitrogen atom is too short-lived to encounter and affix a proton before it converts to the ground state species, radiationlessly. In the acidity range H_0-1 to H_0-5 protonation at the carboxyl group becomes kinetically feasible. However, in this acidity region the doubly charged cation is unstable. As a result, protonation at the carboxyl group results in the ejection of a proton from the protonated ring nitrogen during the lifetime of the excited state. Thus the blue-green fluorescence observed in this acidity region originates from a singly charged cation protonated at the carboxyl group. In support of this hypothesis, the cation derived from 2-naphthoic acid which has an electronic configuration similar to that of quinaldic acid singly protonated at the carboxyl group fluoresces at $2.15 \cdot 10^4$ cm^{-1}[8], an emission very close to that observed for quinaldic acid in the H_0-1 to H_0-5 region. As the sulfuric acid concentration is increased still further, protonation at the ring nitrogen in the excited state, to form the doubly protonated cation, becomes thermodynamically feasible. This would account for the second titration curve and red shift of the fluorescence of quinaldic acid and its methyl ester in very concentrated sulfuric acid solutions. The proposed sequence of events occurring in quinaldic acid in sulfuric acid is represented in Scheme 3.

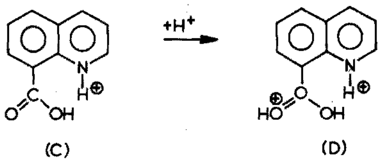
Scheme 3



According to Scheme 3, the midpoints of the fluorimetric titration curves in the region H_0-1 to H_0-5 do not represent simple excited state dissociation constants because tautomerization phenomena are thermodynamically independent of acidity. Rather, they represent the Hammett acidity at which half of the steady-state population of excited singly charged cations protonated at the ring nitrogen, undergoes phototautomerism and half returns to the ground state radiationlessly. On the other hand, the midpoints of the fluorimetric titration curves of quinaldic acid and its methyl ester in the region H_0-5 to H_0-10 are the Hammett acidities at which half of the excited species are present as the singly charged cations, protonated at the carboxyl groups, and half are present as the doubly charged cations. Thus the latter titration midpoints do correspond to pK_a^* values.

The pH dependences of the fluorescences of the species derived from quinoline-8-carboxylic acid are also identical with the pH dependences of the corresponding absorption spectra. Thus it may be concluded that the prototropic conversions of the fluorescences in the pH region are static and that the zwitterion is the uncharged species from which fluorescence originates in near neutral solutions of quinoline-8-carboxylic acid. In the zwitterions of both the 2- and 8-isomers, both the absorption and fluorescence spectra are very much like that of the unsubstituted quinolinium ion, suggesting that in neither zwitterion is the carboxylate group conjugated with the quinoline ring in ground or excited state. Conjugation would be expected to alter appreciably the energy levels and hence the emission spectra of the quinolinium ion. Unlike quinaldic acid, quinoline-8-carboxylic acid shows only a single fluorimetric titration in sulfuric acid. This titration occurs in the less concentrated acid solutions and gives rise to an intense fluorescence which is constant in intensity from H_0-5 to H_0-10 (Fig. 3). The fluorescence in concentrated acid is at higher frequencies than that from any other species derived from the 8-isomer and is in the general region of quinolinium ion fluorescence. The 8-methyl ester fluoresces at lower frequencies than the 8-carboxylate anion while the zwitterion fluoresces at higher frequencies than the anion. Thus it appears that protonation of the exocyclic group, when the ring nitrogen is not protonated, favors conjugation with the quinoline ring in the excited state and hence a lower frequency of fluorescence. However, protonation of the ring nitrogen of the 8-isomer seems to destroy conjugation of the carboxyl group with the aromatic ring in the excited state. Perhaps this is a result of inhibition of charge transfer to the carboxyl group, which must employ its vacant localized molecular orbital to conjugate with the aromatic ring, by the presence of the positive charge residing in the heterocyclic ring of the N-protonated species. In the light of these arguments it is proposed that in the 8-isomer, phototautomerism of the singly charged cation does not occur in sulfuric acid solutions. Rather, the doubly protonated cation (D) is believed to form in the excited state according to Scheme 4 and the presence of the proton at the ring nitrogen in D probably prevents the conjugation of the protonated carboxyl group in the homocyclic ring, accounting for the high frequency of emission of D. The hypothesis of excited state protonation of the carboxyl group of the quinoline-8-carboxylic acid cation is in agreement with the observation of a single fluorimetric titration curve in sulfuric acid.

Scheme 4



The constancy and intensity of the fluorescence of quinoline-8-carboxylic acid in sulfuric acid media (H_0-5 to H_0-10) make fluorimetry an ideal method for the determination of species of known stoichiometry in which this ligand is a complexant. Even in transition metal complexes which are generally nonfluorescent, dissolution in concentrated sulfuric acid would liberate the ligand from the chelates allowing the fluorescence of the ligand to be observed. Similar arguments are applicable to complexes of quinaldic acid. However, the great sensitivity of the quantum yield of fluorescence of quinaldic acid to acidity would no doubt play an important role in determining whether fluorimetry would be a method of choice for quinaldate complexes. At the very least, extremely careful acidity control in standards and unknowns would be required for successful analysis of quinaldates. The fluorescences of both quinaldic acid and quinoline-8-carboxylic acid in the pH range are probably too weak to be of substantial analytical value.

SUMMARY

pH and Hammett acidity dependences of the electronic absorption and fluorescence spectra of quinaldic acid, quinoline-8-carboxylic acid and their methyl esters have been studied. Conversions of the quinoline-like absorption spectra of the anions to quinolinium-like absorption spectra of the uncharged species show that the uncharged ground state species derived from the free acids consist overwhelmingly of the zwitterions. The excited singly charged cation of quinaldic acid appears to undergo an acidity-dependent phototautomerism. However, the 8-isomer does not exhibit this phenomenon. The long emission wavelengths of the esters relative to the zwitterions indicate that of the two electron-withdrawing groups, the carboxyl group is stronger than the heterocyclic nitrogen in the excited state. The fluorescence of quinoline-8-carboxylic acid in sulfuric acid could be very useful for quantitative analysis of transition metal chelates of this ligand.

RÉSUMÉ

Une étude est effectuée sur les équilibres d'ionisation et la spectroscopie électronique (spectres d'absorption et de fluorescence) de l'acide quinaldique, de l'acide quinoléïne-8-carboxylique et de leurs esters méthyliques. La fluorescence de l'acide quinoléïne-8-carboxylique dans l'acide sulfurique pourrait être très utile pour l'analyse quantitative des chélates de métaux de transition de ce ligand.

ZUSAMMENFASSUNG

Die Abhängigkeit der elektronischen Absorptions- und Fluoreszenzspektren von Chinaldinsäure, Chinolin-8-carbonsäure und deren Methylester von der pH- und Hammett-Acidität wurde untersucht. Die Umwandlung der chinolinartigen Absorptionsspektren der Anionen zu den chinoliniumartigen Absorptionsspektren der ungeladenen Spezies zeigt, dass die ungeladenen Grundzustand-Spezies, die sich von den freien Säuren ableiten, überwiegend aus den Zwitterionen bestehen. Das angeregte, einfach geladene Kation der Chinaldinsäure scheint einer aciditätsabhängigen Phototautomerie zu unterliegen. Das 8-Isomere zeigt diese Erscheinung

jedoch nicht. Die langen Emissionswellenlängen der Ester im Vergleich zu den Zwitterionen weisen darauf hin, dass von den beiden elektronenabziehenden Gruppen die Carboxylgruppe stärker als der heterocyclische Stickstoff im angeregten Zustand ist. Die Fluoreszenz der Chinolin-8-carbonsäure in Schwefelsäure könnte für die quantitative Analyse von Übergangsmetall-Chelaten dieses Liganden sehr von Nutzen sein.

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RADIOISOTOPIC X-RAY ANALYSIS

PART II. THE DETERMINATION OF SILVER, TIN AND ANTIMONY IN LEAD

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Energy-dispersive X-ray fluorescence analysis with semiconductor detectors and radioisotopic sources is becoming a valuable alternative to the classical wavelength-dispersive technique in a number of applications. The determination of the most important impurities in lead was investigated with an energy-dispersive configuration incorporating a 45-mCi ^{241}Am source and a small high-resolution Ge(Li) detector as described previously[1]. This detector was 5 mm thick with a surface area of 100 mm^2. At low count rate the pulse-height resolution amounted to 230 eV for the 6.4-keV iron Kα X-rays. This study was intended to investigate the possibility of using the energy-dispersive method for the on-site analysis of lead during or immediately following production. The K-X-radiation of silver, tin and antimony is efficiently excited by the 59.6-keV γ-radiation of the source and the Kα X-radiation is easily resolved with the semiconductor detector. It was, however, to be expected that for accurate determinations, matrix absorption-enhancement effects should be taken into account.

EXPERIMENTAL

A number of lead samples were available with a 28-mm diameter circular cross-section and a thickness of 10 mm. This thickness is large compared with the penetration depth of the exciting and fluorescence radiation. The diameter was considerably larger than the maximum diameter of 12.7 mm allowed in the configuration described previously[1]. A plexiglas sample holder was made to accommodate the lead samples, but owing to the lead collimators before the detector and the source, only a central spot of about 10 mm diameter was effectively excited and measured.

To investigate the reproducibility of the positioning of the sample, one lead sample containing 0.85% of silver was positioned and measured eleven successive times and the reproducibility of the measurement was determined for the silver Kα radiation and the coherently and incoherently scattered 59.6-keV radiation. The results are shown in Table I, whereas similar results for the measurement of silver, antimony and tin in another sample are shown in Table II. As appears from both Tables, the reproducibility of the sample positioning is excellent since the total standard

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* Research associate I.I.K.W.

TABLE I

REPRODUCIBILITY OF THE MEASUREMENTS

Peak or region	Ag Kα	90° scatter	^{241}Am γ
Energy (keV)	22.16	*ca.* 53	59.6
Counts per 30 min (mean)	5,472	131,539	200,964
Total standard deviation	80	766	2080
Standard deviation – counting statistics	74	362	447

TABLE II

REPRODUCIBILITY OF MEASUREMENTS FOR SILVER, ANTIMONY AND TIN

Peak	Ag Kα	Sb Kα	Sn Kβ_1
Energy (keV)	22.16	26.36	28.49
Concentration (%)	0.60	2.12	1.90
Counts per 30 min (mean)	4,431	32,367	6,157
Total standard deviation	116	471	129
Standard deviation – counting statistics	67	180	79

deviation is only slightly higher than could be expected from counting statistics.

For a matrix of high atomic number such as lead, it would be expected that the analysis by X-ray fluorescence would be severely affected by the surface conditions of the samples. Table III shows the results of a number of measurements of the 10.55-keV lead Lα radiation and the coherently scattered primary radiation after various surface polishing and etching procedures, as indicated. The results were largely unaffected by the surface condition of the sample. Moreover, only a thin layer of the sample was effectively analysed. The effective depth which contributed 99% to the measured intensity, was $6.1 \cdot 10^{-2}$ mm for silver, $7.7 \cdot 10^{-2}$ mm for tin, and $8.8 \cdot 10^{-2}$ mm for antimony. To investigate the homogeneity of the samples two samples were

TABLE III

SURFACE TREATMENT OF ONE OF THE LEAD SAMPLES CONTAINING 0.85% SILVER

	Pb Lα (counts/30 min)	*^{241}Am γ (counts/30 min)*
Etched with HNO_3	79,091	207,663
Polished with		
coarse sandpaper (120)	74,634	199,874
emery paper (no. 400)	76,854	202,180
emery paper (no. 600)	76,375	202,290
Al_2O_3 powder	75,172	201,897
Turned off by lathe		
0.1 mm	76,537	198,553
0.2 mm	77,531	201,779
0.3 mm	78,232	202,194

TABLE IV

HOMOGENEITY OF LEAD SAMPLES

Silver concentration (%)	1.98	0.60
Ag Kα (c.p.h. mean)	24,512	7,355
Standard deviation on the mean (%)	0.63	1.73

repeatedly analyzed but a 1-mm layer was removed from the exposed surface before each analysis. The results are shown in Table IV. The sample containing 0.60% silver was much less homogeneous than the one containing 1.98%.

Several standard lead samples were available containing 0.43–0.63% of silver, 0–1.90% of tin and 1.23–2.86% of antimony. The samples were analyzed in the factory by wavelength-dispersive X-ray fluorescence, emission spectrometry and wet chemical analysis[2,3].

As appears from Fig. 1 which shows the X-ray spectrum obtained from a typical sample, the direct determination of tin by means of its Kα radiation is impossible, because of the interference of the Kβ radiation of silver. Hence the $K\beta_1$ line was chosen for tin analysis. For calibration purposes, samples were available which contained silver only, whereas for tin and antimony, the only samples available contained the three elements simultaneously.

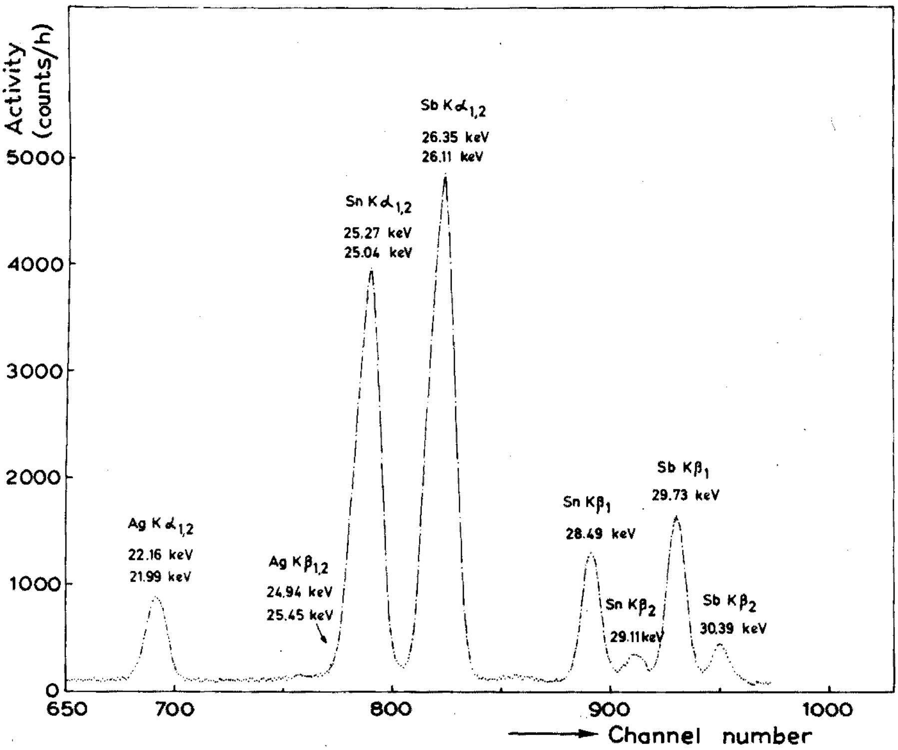


Fig. 1. X-ray spectrum from a lead sample with silver, tin and antimony.

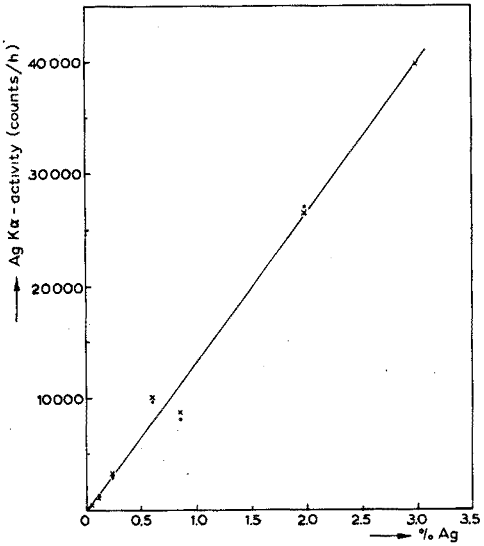


Fig. 2. Calibration curve for only silver present in lead.

The results for silver are shown in Fig. 2. A least-squares analysis of these data yielded a slope of 13,398 ± 56 counts/h/% Ag. The results of a second measurement were obtained after removing a 1-mm layer from the surface. It appears that silver was inhomogeneously distributed in two samples which were discarded for calibration purposes. Absorption effects caused by silver became important above 3% only. Samples containing tin and antimony deviated considerably from this calibration curve and a correction for matrix effects was necessary.

Calibration curves were made for tin on the $K\beta_1$ radiation and for antimony on the $K\alpha$ line (Figs. 3 and 4). For tin no important deviations from linearity were apparent, but considerable deviations occurred for antimony.

From the calibration lines, detection limits were calculated as described by Currie[4]; values of 0.016%, 0.03% and 0.009% were found for silver, tin and antimony, respectively.

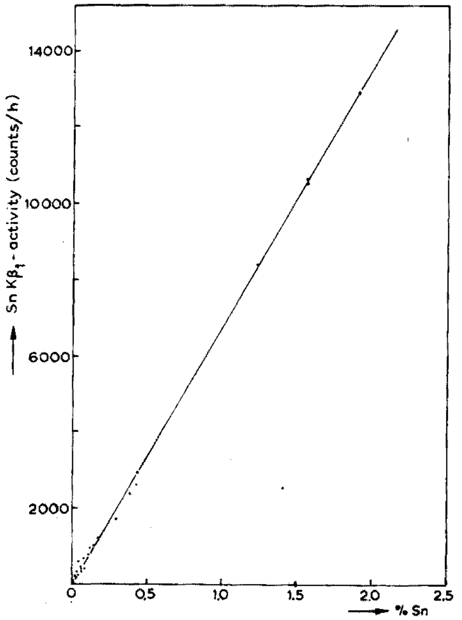
CORRECTIONS FOR MATRIX ABSORPTION

Two methods were used for the correction of inter-element effects. The first was the widely known influence factor method[5] which is based on the equation

$$(I_{Ag})_T = C_{Ag} m_{Ag} = (I_{Ag})_M [1 + C_{Sn} a_{Sn} + C_{Sb} a_{Sb}] \tag{1}$$

where $(I_{Ag})_T$ is the silver activity in the absence of tin and antimony, C_{Ag} is the silver concentration, m_{Ag} is the slope of the calibration curve for pure silver in the matrix and $(I_{Ag})_M$ is the silver activity in the presence of tin and antimony. C_{Sn}, C_{Sb} and a_{Sn}, a_{Sb} are the concentration and influence factors for tin and antimony. Since the mass absorption coefficients for tin and antimony for the silver $K\alpha$ radiation are nearly the same ($\mu_{Sn} = 18.3$, $\mu_{Sb} = 19.4$)[6], a_{Sb} can be equated to a_{Sn} and the equation simplifies to

$$(I_{Ag})_T = C_{Ag} m_{Ag} = (I_{Ag})_M [1 + (C_{Sn} + C_{Sb}) a] \tag{2}$$



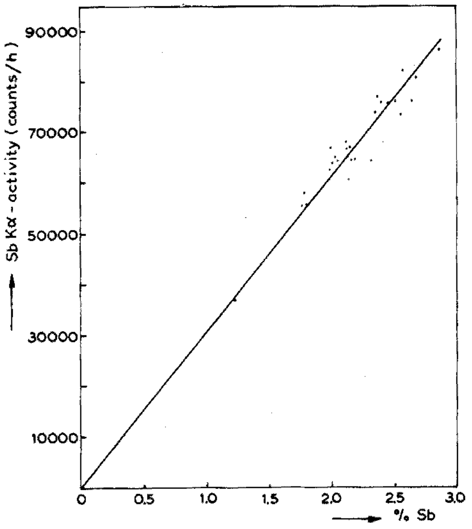


Fig. 3. Calibration curve for tin in lead in the presence of silver and antimony.

Fig. 4. Calibration curve for antimony in lead in the presence of silver and tin.

From the samples available, the value of *a* could be calculated and was found to be equal to -0.033 ± 0.008.

A semi-theoretical method for the correction for matrix absorption was described by Andermann[7], and is equivalent in this case to

$$(I_{Ag})_T = (I_{Ag})_M \exp\left[f\left(C_{Sn} + \frac{\mu_{Sb} - \mu_{Pb}}{\mu_{Sn} - \mu_{Pb}} C_{Sb}\right)\right] \qquad (3)$$

where f is an instrumental factor and μ_{Sn}, μ_{Sb}, μ_{Pb} are the mass absorption coefficients of tin, antimony and lead for the silver Kα radiation. From the same samples, f was calculated and found to be equal to -0.0378 ± 0.0019.

A comparison between the two correction methods used for silver is given in Table V. It can be seen that both methods give values in good agreement with the results based on classical chemical analysis and emission spectrometry. The slope of the straight line obtained after correction with eqn. (2) was 13,682 ± 99 counts/h/% Ag, and 13,595 ± 99 counts/h/% Ag after correction with eqn. (3).

DISCUSSION

The determination of silver, tin and antimony by wavelength-dispersive X-ray fluorescence is practically exclusively based on the use of the L-radiation. The use of this low-energy radiation is precluded here because the resolution of the semiconductor detector is insufficient to resolve the L-radiation of the three metals. Moreover the higher energetic K-radiation is much more effectively excited by the 59.6-keV ^{241}Am source than the L-X-rays, Because of the better penetrability of the high-energy

TABLE V

COMPARISON OF CORRECTION METHODS

Sample number	*% Ag given*	*Corrected with eqn.*(2)	*Error*	*Corrected with eqn.*(3)	*Error*
402	0.60	0.59^4	−0.006	0.58^9	−0.011
413	0.53	0.54^8	+0.018	0.54^5	+0.015
472	0.61	0.59^4	−0.016	0.58^9	−0.021
408	0.59	0.61^0	+0.020	0.60^7	+0.017
410	0.43	0.42^4	−0.006	0.42^1	−0.009
470	0.60	0.64^7	+0.047	0.64^3	+0.043
466	0.61	0.61^2	+0.002	0.60^7	−0.003
483	0.62	0.62^9	+0.009	0.62^4	+0.004
403	0.60	0.60^7	+0.007	0.60^3	+0.003
399	0.55	0.61^8	+0.068	0.61^5	+0.065
473	0.63	0.62^0	−0.010	0.61^5	−0.015
469	0.60	0.65^8	+0.058	0.65^4	+0.054
467	0.62	0.62^5	+0.005	0.62^0	—
412	0.54	0.53^8	−0.002	0.53^5	−0.005
396	0.57	0.56^6	−0.004	0.56^2	−0.008
398	0.57	0.59^0	+0.020	0.58^6	+0.018
397	0.58	0.57^3	−0.007	0.57^0	−0.010
406	0.59	0.58^8	−0.002	0.58^5	−0.005
421	0.55	0.57^3	+0.023	0.57^0	+0.020
468	0.60	0.59^6	−0.004	0.59^3	−0.007
401	0.56	0.58^8	+0.028	0.58^4	+0.024
409	0.59	0.60^8	+0.018	0.60^5	+0.015
414	0.54	0.54^4	+0.004	0.54^1	+0.001
471	0.60	0.63^3	+0.033	0.62^9	+0.029
8005	0.59	0.59^6	+0.006	0.59^2	+0.002

radiation a thicker surface layer of the lead sample is analysed. This should lead to a higher sensitivity and perhaps to a lesser dependence of the analytical results on the surface condition of the samples and on inhomogeneities of the impurities throughout the matrix.

The correction methods for interelement effects applied here to the determination of silver should also be applicable to the determination of tin and antimony. No samples were available with a sufficient concentration range to obtain meaningful data.

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SUMMARY

A 90° symmetry arrangement for the determination of silver, tin and antimony in pure lead by means of an energy-dispersive X-ray fluorescence spectrometer with ^{241}Am as excitation source is described. Two correction methods for matrix absorption are used.

RÉSUMÉ

On propose une méthode de dosage de l'argent, de l'étain et de l'antimoine dans un plomb pur, par spectrométrie de fluorescence aux rayons-X, en utilisant ^{241}Am comme source d'excitation. On dispose de deux méthodes de correction pour l'absorption de la matrice.

ZUSAMMENFASSUNG

Eine 90° Symmetrie-Anordnung wird beschrieben für die Bestimmung von Silber, Zinn und Antimon in reinem Blei mittels eines energieauflösenden Röntgenfluoreszenz-Spektrometers. Für die Anregung wird ^{241}Am verwendet. Die Matrixabsorption wird nach zwei Methoden korrigiert.

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THE DETERMINATION OF RHENIUM IN FLUE DUST BY NEUTRON ACTIVATION ANALYSIS

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There is an increasing economic interest in rhenium, *e.g.* in the field of catalysis. Rhenium is, however, one of the least abundant elements; in addition, it is a dispersed element in the sense that it occurs almost entirely in minerals of other elements. Because of the low concentrations invariably involved, sensitive methods are required for its determination. Neutron activation analysis is quite appropriate, because of the high activation cross-sections of both the naturally occurring isotopes and the favorable resulting half-lives.

Neutron activation has been used to determine rhenium in various and complex matrices, as appears from the bibliography by Lutz *et al.*[1]. Gureev *et al.*[2] determined down to 10 p.p.m. rhenium after activation with a Po–Be neutron source and radiochemical purification. The same authors reported the nondestructive determination of 100 p.p.m. rhenium in molybdenites by reactor irradiation and γ-ray spectrometry, while Graber *et al.*[3] discussed the possibilities of Ge(Li) detectors for this purpose. The above concentrations are, however, within the possibilities of classical methods such as spectrophotometric determination (*e.g.* the detection limit of the rhenium(IV)–thiocyanate method is 0.1–0.5 p.p.m.). Hence activation with reactor neutrons, followed by radiochemical separation, is of more practical interest, since lower rhenium contents can be determined. Usually a known amount of inactive rhenium carrier is added to the sample after irradiation, which allows the chemical yield to be determined, *e.g.* by reactivation. Radiochemical neutron activation analysis has successfully been applied to such materials as meteorites[4–10], tektites[11], rocks[12–17] including lunar material[18], geochemical standards[19], ores such as molybdenites[20–25], columbite[26], copper ores[27], industrial products such as electrolytic zinc sulfate solutions[28], high-purity materials[29] such as silicon carbide[30] and gallium arsenide[31], organic material such as enzymes, marine biological organisms and ashes[32–35], and trichloromethylsilane[36].

In the above analyses rhenium was separated by precipitation as sulfide, tetraphenylarsonium perrhenate or nitron perrhenate, by extraction with quaternary ammonium or arsonium salts, by distillation usually from hydrobromic–sulfuric acid medium, and by anion exchange. An interesting alternative is the substoichiometric separation after irradiation. The substoichiometric extraction of perrhenate with tetraphenylarsonium chloride has been described by Perezhogin[37] and

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Kormanova[38], and with rhodamine B hydrochloride in nitrobenzene by Doctor and Haldar[39].

In this work, rhenium was determined by radiochemical neutron activation analysis in some industrial concentrates, namely various types of flue dust from the processing of copper ores. The products studied contained high concentrations of Mg, Al, Si, Fe, Co, Zn, Cd, As, Sb, Pb and/or copper (*e.g.* up to 30% copper), but were low in molybdenum. Two approaches were used in the post-irradiation radiochemical separation: (*a*) distillation from perchloric–hydrochloric acid solution and (*b*) hydroxide scavenging followed by extraction with tetraphenylarsonium chloride in chloroform. For high concentrations ($\geqslant 1$ p.p.m.), the results were compared with spectrophotometric determinations, carried out in an industrial laboratory.

The separation procedure was previously tested by radioactive tracer techniques.

EXPERIMENTAL

Radioactive tracer study

Extraction of $(C_6H_5)_4AsReO_4$ *in chloroform.* Flue dust samples (0.5–1 g) were fused with 5 g of sodium peroxide in a nickel crucible, in the presence of $^{186+188}$Re tracer (50 μg Re/50 μl). After cooling, the cake was disintegrated with water in a 500-ml beaker, covered with a watch glass, and the crucible was rinsed with a minimal volume of 6 *M* hydrochloric acid. The remaining precipitate (A) was separated by centrifugation, washed three times with 10 ml of water, and discarded. The supernate was acidified with 7.5 *M* and 1 *M* sulfuric acid to pH 7. The hydroxide precipitate (B) was filtered off, washed with water, and discarded. To the filtrate 10 mg of tetraphenylarsonium chloride was added and $(C_6H_5)_4AsReO_4$ was extracted twice with 10 ml of chloroform.

Counting of the various fractions showed that usually 10–20% of the rhenium was absorbed in precipitate A, 1% in precipitate B and 0.1% in the aqueous phase after extraction. Chemical yields of 80–90% are thus expected.

Distillation from perchloric–hydrochloric acid solution. After peroxide fusion, cooling and disintegration of the cake (as described above), the solution was transferred to a distillation flask and acidified with 8 ml of 7.5 *M* sulfuric acid and 50 ml of 70% perchloric acid. A clear solution was obtained. A slow current of air was aspirated through the distillation train, while heating the distillation flask. The fraction distilled below 150° was discarded (distillation time 1–2 h). From a slowly dropping funnel, concentrated hydrochloric acid was then added to the distillation flask, and the rhenium distillate was collected in 10 ml of ice-cooled water (distillation time: 30–45 min).

Tracer experiments showed that the chemical yield was typically 60–90%. Usually 0.5% rhenium was lost in the fore-run, whereas 40–10% remained in the residue.

Nuclear data

In Table I, the nuclear data for neutron activation of rhenium are summarized.

The following interfering nuclear reactions could be neglected, as the tungsten, osmium and iridium content of the flue dust samples was insignificant and as irra-

TABLE I

NUCLEAR DATA

Natural isotope	*Isotopic abundance (%)*	*Thermal neutron cross-section (barn)*	*Isotope formed*	*Half-life*	*Main γ-transition energies in keV (no. of γ-quanta per 1000 decays)*
^{185}Re	37.07	110	^{186}Re	90 h	137.0 (146); 641.5 (1); 767.3 (1) W, Os X-rays
^{187}Re	62.93	72	^{188}Re	16.7 h	155.03 (899); 478.0 (58); 633.0 (82); 829.0 (23); 932.0 (34) + others Os X-rays
		2	^{188m}Re	18.7 min	92.4 (52); 105.8 (104) Re X-rays

diations were carried out at a relatively low and well thermalized neutron flux ($\phi_{th} = 5 \cdot 10^{11}$ n cm^{-2} s^{-1}); ^{184}W(n,γ)^{185}W $\xrightarrow{\beta^-}$ ^{185}Re(n,γ)^{186}Re; ^{186}W(n,γ)^{187}W $\rightarrow$ $\xrightarrow{\beta^-}$ ^{187}Re(n,γ)^{188}Re; ^{184}Os(n,γ)^{185}Os $\xrightarrow{E.C.}$ ^{185}Re(n,γ)^{186}Re; ^{186}Os(n,p)^{186}Re; ^{188}Os(n,p)^{188}Re; ^{191}Ir(n,α)^{188}Re.

Irradiation and counting

Flue dust samples (100–500 mg) were weighed and sealed in polyethylene vials. Standards were obtained by spotting 50 μl (5 μg Re) of an ammonium perrhenate solution (Johnson Matthey, "specpure") on 1 cm^2 of Whatman filter paper. They were irradiated together with the samples at a neutron flux of $5 \cdot 10^{11}$ n cm^{-2} s^{-1} for 6 h in the reactor Thetis.

After cooling for 36 h, 100 μg of rhenium (50 μl of an ammonium perrhenate solution) were added to samples and standards, before sodium peroxide attack. Rhenium was separated by the methods described above and the purified fractions were counted in glass vials for 30 min to 5 h, with a 4000-channel analyzer coupled to a low-energy photon Ge(Li) detector. This detector has been described elsewhere[40]; it has an active volume of *ca.* 0.4 cm^3, and a resolution of 245-eV FWHM at the 6.40-keV Fe $K_{\alpha(1+2)}$ X-ray. Activities were determined by integrating the 137.0-keV peak of ^{186}Re and/or the 155.0-keV peak of ^{188}Re.

In addition, the different fractions of the separations were counted with a conventional Ge(Li) detector (40 cm^3, FWHM = 2.2 keV at 1332.4 keV) in order to study the decontamination obtained by the two separation methods being used.

Chemical yield determination

Chemical yields were obtained by reactivation. The chloroform phases were diluted to 50 ml, and 200 μl was transferred to a polyethylene vial and evaporated. The distillates were diluted to 100 ml, and 100 μl was absorbed on 50 mg of silica, but not evaporated, as losses of rhenium can occur when solutions containing perchloric acid are evaporated. Reactivation was carried out at a neutron flux of $5 \cdot 10^{11}$ n cm^{-2} s^{-1} for 2 h, in the presence of standards (0.5 μg Re). Countings were performed one day after irradiation with the low-energy photon detector, and the 155.0-keV peak of 16.7-h ^{188}Re was used for the yield determination.

RESULTS

In the chloroform phases, the only contaminant observed with the low-energy photon detector in the energy range from 10–200 keV, was 6.01-h ^{99m}Tc (daughter nuclide of ^{99}Mo). The 140-keV peak of ^{99m}Tc was well resolved from the 137-keV peak of ^{186}Re, as appears from Fig. 1. When a detector of inferior resolution is used, it is better to measure the 155-keV peak of ^{188}Re, or to wait for the decay of ^{99m}Tc; because of the low molybdenum content of the present samples, the ^{99m}Tc contamination was quite small. The peaks in the 30–40-keV region were due to the fluorescence of barium present in the glass vials; those at 67.0, 68.8 and 77.9 keV were due to fluorescence of gold, used as an electrode in the detector[40].

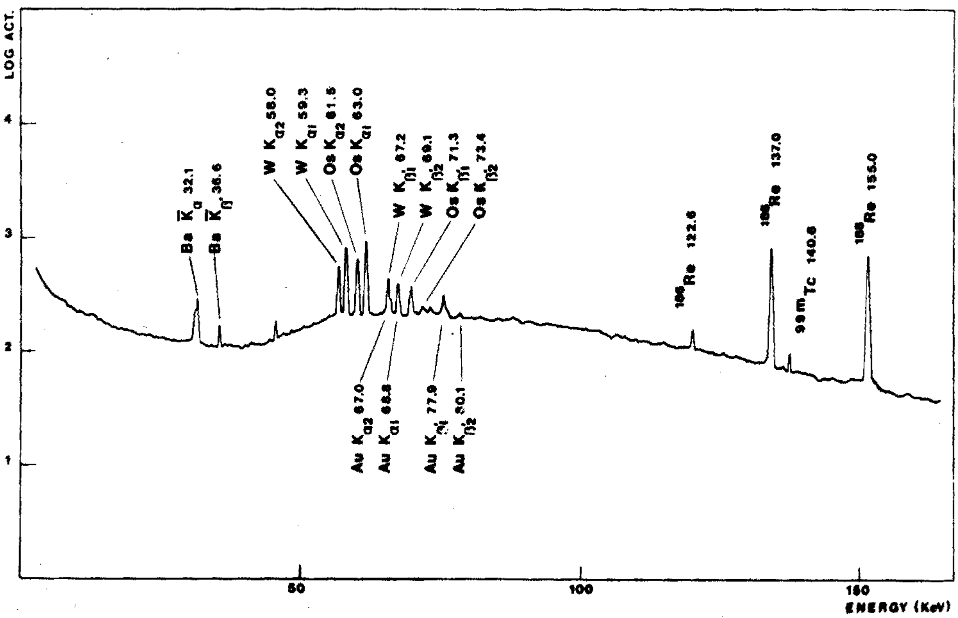

Fig. 1. γ-Ray spectrum of ^{186}Re + ^{188}Re separated from flue dust sample 4, containing 0.98 μg of rhenium, measured for 14 h with a Ge(Li) low-energy photon detector after 5 days cooling.

The distillates showed no radiochemical contamination with the low-energy photon detector although it should be noted that they were usually observed after a longer waiting time, because of the more time-consuming distillation procedure.

The various fractions obtained after chemical separation were measured with a 40-cm^3 Ge(Li) detector. It appeared that precipitate A was effective in removing the activities of Sb, Cd, Co, Cu and Zn (^{122}Sb, ^{124}Sb, ^{115}Cd, ^{60}Co, ^{64}Cu, ^{65}Zn), whereas precipitate B removed As (^{76}As), and additional copper and zinc activities (^{64}Cu, ^{65}Zn). The chloroform phase was still slightly contaminated with ^{64}Cu, ^{76}As and ^{82}Br. In the distillates, small amounts of ^{51}Cr and ^{76}As were sometimes detected.

Table II shows the results of the neutron activation determination of rhenium in flue dust samples. For comparison, the results of a spectrophotometric determination are also listed. Except for sample 5, the agreement with the neutron activation

TABLE II

RHENIUM CONTENT OF FLUE DUST SAMPLES (IN p.p.m.)

Sample number	*NAA distillation*	*NAA extraction*	*Spectrophotometry*[a]
1	—	0.063	< 0.5
		0.042	
2	—	0.166	< 0.5
		0.132	
3	—	0.77	< 0.5
		0.76	
4	0.95	0.91	0.87
	1.05	1.00	
5	18.4	17.3	12
6	108	112	103

[a] The sample was attacked with a sodium peroxide + sodium hydroxide fusion, the melt disintegrated in water, the filtrate treated with citric acid, and rhenium extracted as tetraphenylarsonium complex into hexone. Rhenium was then converted to the thiocyanate complex by shaking with an aqueous solution containing tin(II) chloride and ammonium thiocyanate. The coloured Re–SCN complex was measured in the organic phase at 430 nm.

results is satisfactory, although the colorimetric method has a tendency to give lower results; there is, indeed, no way to correct for losses during the various separation steps. The two separation procedures used in the neutron activation determination yield the same results; the extraction method is, however, less time-consuming, and is preferred by the present authors.

SUMMARY

Rhenium was determined by radiochemical neutron activation analysis in flue dust samples of complex chemical composition. Two separation techniques were used: distillation from perchloric–hydrochloric acid solution and hydroxide scavenging followed by extraction with tetraphenylarsonium chloride in chloroform. ^{186}Re and ^{188}Re were measured with a Ge(Li) low-energy photon detector. Chemical yields were determined by reactivation. For a neutron flux of $5 \cdot 10^{11}$ n cm^{-2} s^{-1}, an irradiation time of 6 h and samples of *ca.* 1 g, down to 50 p.p.b. of rhenium could be determined.

RÉSUMÉ

Le rhénium est dosé par analyse radiochimique par activation neutronique dans des échantillons de poussière, de composition chimique complexe. Deux techniques de séparation sont utilisées: distillation de solutions acide chlorhydrique–acide perchlorique et extraction au moyen de chlorure de tétraphénylarsonium dans le chloroforme. ^{186}Re et ^{188}Re sont mesurés à l'aide d'un détecteur Ge(Li). On peut doser ainsi jusqu'à 50 p.p.b. de rhénium au minimum avec un flux de neutrons de $5 \cdot 10^{11}$ n cm^{-2} s^{-1}, un temps d'irradiation de 6 h et des échantillons d'environ 1 g.

ZUSAMMENFASSUNG

Rhenium in Flugstaubproben komplexer chemischer Zusammensetzung wurde durch radiochemische Neutronenaktivierungsanalyse bestimmt. Es wurden zwei Trennverfahren angewendet: Destillation aus perchlor-salzsaurer Lösung und Hydroxid-Mitreissfällung mit anschliessender Extraktion mit Tetraphenylarsoniumchlorid in Chloroform. ^{186}Re und ^{188}Re wurden mit einem Ge(Li)-Photonendetektor für niedrige Energien gemessen. Die chemischen Ausbeuten wurden durch Reaktivierung ermittelt. Bei einem Neutronenfluss von $5 \cdot 10^{11}$ n cm^{-2} s^{-1}, einer Bestrahlungszeit von 6 h und Proben von *ca.* 1 g konnte Rhenium bis zu 50 p.p.b. herab bestimmt werden.

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THE DETERMINATION OF IRON IN IRON ALLOYS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Iron is the major element in ferrous alloys, and traditionally it is not determined. Classical methods, when used, have involved precipitation with ammonia, followed by titration with EDTA[1], chromium(VI)[2], or cerium(IV)[3]. Rotating disk optical emission spectrography was used by Waggoner[4] for 70% (s_r, 0.012).

Atomic absorption spectrophotometry is used widely for the determination of alloying elements in ferrous alloys and various interferences may be encountered. These analyses require a calibration series which adequately resembles the physical and chemical characteristics[5,6] of the solution being analysed, and the use of background measurement corrections[6–8]. Accordingly, a need has arisen for a rapid and sufficiently accurate analysis of the iron concentration, particularly of unknown ferrous alloys, so that adequate calibration series may be prepared for alloying element analyses.

Minor amounts of iron in a variety of inorganic materials have been determined by atomic absorption spectrophotometry[9]; the air–acetylene flame has been recommended and silicon interference has been reported[10,11].

Two relevant investigations of nickel-base alloys are the determination of up to 20% iron (s_r, 0.01) in a 0.5% (w/v) hydrochloric–hydrofluoric acid solution, at the 248.3-nm line[12], and up to 2% iron (s_r, 0.03) in hydrochloric acid solutions at the 372.0-nm line[13].

For the present need to determine 50–100% iron, it was convenient to investigate the applicability of the usual preparative media of 0.5–2% (w/v) hydrochloric[14–17], and 0.5–1% (w/v) phosphoric–sulphuric acids[17–19], which are used for the analysis of alloying elements in iron alloys by atomic absorption spectrophotometry.

EXPERIMENTAL

Apparatus

A Varian-Techtron atomic absorption spectrophotometer AA4 with digital readout was used with an AB41 burner (100 × 0.5 mm), and high-intensity iron hollow-cathode lamp (primary current, 15 mA; booster current, 300 mA).

Reagents

Iron rod. Johnson and Matthey spectrographically standardized. Fine turnings were prepared on a lathe with a tungsten carbide tipped tool.

Recommended procedures

Hydrochloric acid media. Weigh a 2-, 1- or 0.5-g sample[14-17] into a 250-ml conical beaker, and also iron turnings for a calibration series covering the range 50–100% iron. Dissolve with 30 ml of 50% (v/v) hydrochloric acid (1 g–20 ml, 0.5 g–15 ml) and oxidize with 2–5 ml of nitric acid (s.g. 1.42). Evaporate to dryness and bake at 150°. Cool, extract with 15 ml of hydrochloric acid (s.g. 1.18), and warm gently until salts are dissolved. Add 30 ml of water, digest for 5 min and filter through a medium paper into a 100-ml graduated flask. Rinse the beaker and paper ten times with 5% (v/v) hydrochloric acid and dilute to the mark with water.

Phosphoric–sulphuric acid media. Weigh a 1- or 0.5-g sample[17-19] into a 125-ml conical beaker, and also iron turnings for a calibration series covering the range 50–100% iron. Dissolve with 30 ml of 15% (v/v) phosphoric–15% (v/v) sulphuric acid; the solution of some highly-alloyed materials can be assisted by the addition of aqua regia. Oxidize with 1–3 ml of nitric acid (s.g. 1.42), evaporate to fumes and fume for 1 min. Cool, extract with 30 ml of water, add 5 drops of 6% (w/v) sulphurous acid, and digest for 5 min to resolve all soluble salts. Filter through a medium paper into a 100-ml graduated flask. Rinse the beaker and paper ten times with 2% (v/v) sulphuric acid and dilute to the mark with water.

Measurement. Measure the absorbance at 376.7 nm (1 and 2% (w/v) hydrochloric acid media), or 392.0 nm (1 and 0.5% (w/v) phosphoric acid–sulphuric acid and 0.5% (w/v) hydrochloric acid media) using a very lean air–acetylene flame (5.5 $\mathrm{l\,min^{-1}}$ air at 170 $\mathrm{kNm^{-2}}$ and 1.3 $\mathrm{l\,min^{-1}}$ acetylene at 70 $\mathrm{kNm^{-2}}$ and an absorption path 6 mm above the burner top.

RESULTS AND DISCUSSION

Iron determinations (50–100% Fe) are required mainly for the preparation of matrix-matched calibration solutions (nearest 5–10% Fe) for minor alloying element analyses. Accordingly, less-sensitive absorption lines of iron are worthy of investigation, so that the solution prepared for the minor alloy analyses[14-19] may be used without dilution. The precision and accuracy of iron determinations required for the preparation of calibration solutions are less than those required for referee analyses; nevertheless, it was useful to investigate the ultimate precision and accuracy which could be obtained from an atomic absorption procedure for the determination of iron in iron alloys.

The most sensitive (1% $T \approx 0.1$ $\mu\mathrm{g\,ml^{-1}}$) absorption line of iron when using a 100-mm burner is 248.3 nm[20-23]; however, the sensitivity under conditions of minimal interference by other elements (very lean flame) is reduced to 0.2 $\mu\mathrm{g\,ml^{-1}}$. This allows a maximal working concentration range (taken as 200 × sensitivity) of 0–40 μg Fe $\mathrm{ml^{-1}}$ in hydrochloric acid media and 0–50 μg Fe $\mathrm{ml^{-1}}$ in the more viscous and less sensitive phosphoric–sulphuric acid media. However, if burner rotation, as a method of reducing sensitivity, is avoided in the interests of best precision, then the working concentration ranges (mg $\mathrm{ml^{-1}}$) required for the analyses of 50–100% iron respectively are 10–20 (2 g), 5–10 (1 g) and 2.5–5 (0.5 g), and the absorption sensitivities (1% T) required would not exceed 200, 100 and 50 $\mu\mathrm{g\,ml^{-1}}$. Absorption sensitivities ranging from 0.1 $\mu\mathrm{g\,ml^{-1}}$ (248.3 nm) to approximately 20 $\mu\mathrm{g\,ml^{-1}}$ (392.0 nm) have been reported for 21 lines[9,21,22], but with minimal interference conditions these sensitivities would approximate to the range 0.2–40 μg ml^{-1}. Accordingly, for all reported lines, only 392.0 nm appeared to have application to the present investigation, and a search for further suitable lines was required.

All iron lines not reported previously in the atomic absorption literature, but with a lower energy level commencing in the ground state and an emission intensity greater than 34[20] were tested for atomic absorption sensitivity. All were found to be too sensitive for the desired application. Of the 21 lines previously reported in the atomic absorption literature[9,21,22], only seven do not have a lower energy level commencing in the ground state; of these the line with the maximal lower energy level (978 K) was 392.0 nm[20].

A further 21 lines, not previously reported in atomic absorption literature and with lower energy transitions in the range 416–12,969 K and emission intensities in the range 36–400[20], were tested for atomic absorption sensitivity; experimental conditions which indicated the sensitivity under conditions of minimal interferences and maximal sensitivity were established. The results obtained under maximal sensitivity conditions, and with two typical solution concentrations are recorded in Table I. For the present application, 346.59, 357.01, 360.89, 361.88, 363.15, 375.82, 376.72, 382.78, 388.63 and 392.03 nm were selected for more extensive testing.

TABLE I

ATOMIC ABSORPTION SENSITIVITIES OF IRON LINES IN HYDROCHLORIC AND PHOSPHORIC–SULPHURIC ACID MEDIA

λ (nm)	*Sensitivity (μg ml^{-1})*		*λ (nm)*	*Sensitivity (μg ml^{-1})*	
	0.5% (w/v) Fe–15% (v/v) HCl	*1.0% (w/v) Fe–4.5% (v/v) H_3PO_4–4.5% (v/v) H_2SO_4*		*0.5% (w/v) Fe–15% (v/v) HCl*	*1.0% (w/v) Fe–4.5% (v/v) H_3PO_4–4.5% (v/v) H_2SO_4*
247.98	7	9	382.59	10	12
248.98	2	3	382.78	40	50
346.59	12	14	388.63	14	16
357.01	40	50	392.03	40	50
360.89	35	50	404.58	300	350
361.88	30	40	406.36	600	700
363.15	35	45	407.17	1100	1300
374.56	6	8	427.18	750	1000
375.82	25	30	430.79	700	900
376.72	140	160	438.36	300	350
381.58	300	400			

After intensive evaluation, 376.72 nm was selected for the 2% and 1% (w/v) methods in hydrochloric acid media, and 392.03 nm for the 0.5% (w/v) method in hydrochloric acid media and 1% and 0.5% (w/v) methods in phosphoric–sulphuric acid media. Calibration curves for determinations in the range 50–100% iron necessitate a decision whether to use solutions of varying iron concentration which contain only the element sought, or to build up a complex set of calibration solutions of constant cation concentration with varying amounts of iron and alloying elements which reflect the alloy compositions being analysed. For a general purpose method, the former will give more pronounced curvature of the calibration graph to the concentration axis and a lowered accuracy, whereas the latter is more suitable if known specific alloy types are being analysed.

A calibration series containing iron only was selected. The resulting calibration curves were regularly depressed towards the concentration axis, the degree of depression being more pronounced with the more viscous phosphoric–sulphuric acid solutions. The iron sensitivities with the selected acid media, sample weights and wavelengths, together with the extent of curvature when using a very lean air–acetylene flame, are shown in Table II. With the calibration method selected, then for any particular iron concentration in a sample being analysed, two interference effects can be present simultaneously: one is depression caused by increasing solution viscosity as the iron concentration increases, and the other is variation in the population of iron atoms at the lower energy level as a function of the influence of alloying elements present.

No significant interference effects were experienced from 10% Mn or from 5% Mo, V, Cu, Co or Al, when a very lean air–acetylene flame was used. Three elements, chromium, nickel and tungsten, caused significant interference which was minimal with the very lean air–acetylene flame. Because of the calibration method selected, the level of interference varies with the iron concentration and the sum total of interfering elements, being progressively slightly higher as the iron concentration increases.

TABLE II

THE VARIATION OF IRON SENSITIVITY AS A FUNCTION OF ACID MEDIA, IRON CONCENTRATION, SAMPLE WEIGHT AND WAVELENGTH

Sample size (g)	*Solution concentration*	*λ (nm)*	*Sensitivity (1% T-µg ml^{-1})*	
			50% Fe	*100% Fe*
2	2.0% (w/v) Fe–15% (v/v) HCl	376.72	196	218
1	1.0% (w/v) Fe–15% (v/v) HCl	376.72	180	197
0.5	0.5% (w/v) Fe–15% (v/v) HCl	392.03	56	59
1	1.0% (w/v) Fe–4.5% (v/v) H_3PO_4–4.5% (v/v) H_2SO_4	392.03	56	67
0.5	0.5% (w/v) Fe–4.5% (v/v) H_3PO_4–4.5% (v/v) H_2SO_4	392.03	47	56

TABLE III

INTERFERENCE LEVEL OF CHROMIUM, NICKEL AND TUNGSTEN AT 70% IRON CONCENTRATION

Sample	*Solution concentration*	*λ (nm)*	*Depressive interference-% Fe*		
			/1% Cr	*/1% Ni*	*/1% W*
2	2.0% (w/v) Fe–15% (v/v) HCl	376.72	0.05	0.01	n.a.[a]
1	1.0% (w/v) Fe–15% (v/v) HCl	376.72	0.03	0.01	n.a.
0.5	0.5% (w/v) Fe–15% (v/v) HCl	392.03	0.02	0.005	n.a.
1	1.0% (w/v) Fe–4.5% (v/v) H_3PO_4–4.5% (v/v) H_2SO_4	392.03	0.125	0.15	0.065
0.5	0.5% (w/v) Fe–4.5% (v/v) H_3PO_4–4.5% (v/v) H_2SO_4	392.03	0.10	0.125	0.060

[a] n.a. = not applicable.

TABLE IV

IRON CONTENT OF STANDARD IRON AND STEELS AND TWO CALIBRATION POINTS

Sample	*Alloy elements* (%)	% *Fe* (*Diff.*)	% *Iron found*[a]				
			376.7 *nm*		392.0 *nm*		
			2% *w/v* (*HCl*)	1% *w/v* (*HCl*)	0.5% *w/v* (*HCl*)	1% *w/v* (H_3PO_4–H_2SO_4)	0.5% *w/v* (H_3PO_4–H_2SO_4)
NBS 153	8Mo, 8Co, 4Cr, 2V, 2W	73.8	73.1 (0.2) (0.7)	72.9 (0.4) (0.9)	74.1 (0.4) (0.3)	73.5 (0.2) (0.3)	73.0 (0.2) (0.8)
BCS 149/2	—	99.8	99.9 (0.1) (0.1)	99.8 (0.4) (0.1)	99.7 (0.4) (0.2)	99.7 (0.4) (0.1)	99.6 (0.4) (0.2)
NBS 341	20Ni, 2Co, 2C, 1Mn	72.1	71.5 (0.4) (0.6)	72.0 (0.4) (0.1)	72.7 (0.3) (0.6)	71.6 (0.3) (0.5)	71.6 (0.4) (0.5)
BCS 290	13 Mn	85.3	84.9 (0.2) (0.4)	85.3 (0.5) (0.0)	85.2 (0.4) (0.1)	84.1 (0.3) (1.2)	84.2 (0.4) (1.1)
NBS 101d	19 Cr, 9 Ni	70.4	69.1 (0.1) (1.3)	70.5 (0.3) (0.1)	70.8 (0.2) (0.4)	71.0 (0.1) (0.6)	70.0 (0.3) (0.4)
NBS 50 c	18 W, 4 Cr, 1 V	74.5	n.a.[b]	n.a.	n.a.	74.2 (0.3) (0.3)	74.4 (0.3) (0.1)
75% Fe	—	75.0	74.5 (0.3) (0.5)	74.9 (0.7) (0.1)	74.6 (0.3) (0.4)	75.8 (0.2) (0.8)	75.0 (0.6) (0)
95% Fe	—	95.0	94.6 (0.3) (0.4)	95.8 (0.4) (0.8)	94.8 (0.6) (0.2)	95.0 (0.3) (0)	95.0 (0.4) (0)

[a] The numbers given in parentheses after each result are the standard deviation for 6 determinations, and ΔFe, which is the deviation between calculated iron result and mean of determinations without respect to sign.

[b] n.a. = not applicable.

The general level of interference at 70% iron concentration is shown in Table III; these levels are dependent upon, and would vary somewhat with, the particular instrument used.

Some workers use shorter preparation procedures than those indicated under recommended procedure; some[19,24] dilute to volume immediately after sample dissolution without filtration, whilst others impose a filtration step without a baking or fuming treatment[17,25-27]. These techniques would lead to poorer precision and accuracy, owing to soluble silicon interference, and varying iron absorption by partly dehydrated silicic acid. Whilst these shorter preparation procedures can be useful for the rapid analysis of minor elements, they are not applicable to precise iron determinations.

A series of plain and highly alloyed irons and steels together with two calibration points (75 and 95% Fe) treated as unknown samples, were analysed by the proposed procedure. As indicated in the introduction, standard steels are not supplied with a certificated analysis for total iron, although the iron concentration as determined by difference is sufficiently accurate for this evaluation, provided that an extensive certificated alloy analysis is given and a small allowance (*ca.* 0.1%) is made for the gas content. The results obtained (Table IV) show that the procedures developed can be applied to the determination of iron in iron alloys with the reported results being ±1% abs. of the calculated result. Within this context, there are no significant deviations in accuracy or precision, when the proposed methods are applied to simple or highly alloyed irons and steels or when hydrochloric acid or phosphoric–sulphuric acid media are used. The proposed procedures are also directly applicable to the preparation of matrix-matched calibration solutions for the analysis of minor elements in ferrous alloys without the necessity for a separate preparative solution of the sample being analysed.

Appreciation is expressed to The Broken Hill Proprietary Company Limited for permission to publish this work.

SUMMARY

A study was made of the determination of 50–100% iron in iron alloys by atomic absorption spectrophotometry. The procedure developed is applicable to preparing matrix-matched calibration curves for the direct determination of minor elements in ferrous alloys and to the determination of the alloying concentration of iron in alloys. Chromium, nickel and tungsten cause a small depressive interference and a very lean air–acetylene flame provides conditions of minimal interference. Hydrochloric or phosphoric–sulphuric acid media are recommended for three different sample weights and the 376.7- and 392.0-nm wavelengths. Results are presented for standard samples and the precision data indicate that results which are within 1% of the expected result can be obtained.

RÉSUMÉ

Une méthode est mise au point pour le dosage du fer dans ses alliages (50 à 100% Fe), par spectrophotométrie d'absorption atomique. Le chrome, le nickel et le tungstène causent une faible interférence dépressive. Les milieux acide chlorhydrique ou acides phosphorique–sulfurique sont recommandés, ainsi que les longueurs d'onde 376.7 et 392.0 nm. Les résultats de divers échantillons standards sont donnés; on arrive à des résultats de ±1 % des valeurs attendues.

ZUSAMMENFASSUNG

Es wurde eine Untersuchung über die Bestimmung von 50–100 % Eisen in Eisenlegierungen durch Atomabsorptionsspektrophotometrie durchgeführt. Das entwickelte Verfahren eignet sich für die Aufstellung von matrixangeglichenen Eichkurven für die direkte Bestimmung von Nebenbestandteilen in Eisenlegierungen und die Bestimmung der Legierungskonzentration von Eisen in Legierungen. Chrom, Nickel und Wolfram verursachen eine kleine negative Abweichung, und eine sehr magere Luft–Acetylen-Flamme ist die Bedingung für minimale Störung. Salzsaure oder phosphor–schwefelsaure Lösungen werden für drei verschiedene Probeneinwaagen empfohlen sowie die Wellenlängen 376.7 und 392.0 nm. Die Ergebnisse für Standardproben werden vorgelegt, und der Wert der Reproduzierbarkeit weist daraufhin, dass Ergebnisse erhalten werden können, die innerhalb ±1 % des erwarteten Ergebnisses liegen.

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SPECTROPHOTOMETRIC DETERMINATION OF THE NUMBER OF ABSORBING SPECIES IN SOLUTION

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The determination of the number of absorbing species in solution is one of the basic problems of the analytical chemistry of solutions. It has been solved many times by various authors. A recent solution to the problem and a list of previous papers in the area has been published by Coleman *et al.*[1]. All previous work is based on relatively complicated matrix theory and the results are presented in a form that is not usual in analytical chemistry.

In this paper a simple method of developing the final equations in a more analytically usual form is presented.

EXPERIMENTAL

Apparatus

All photometric measurements were made with a double-beam Cary 14 (Monrovia, Calif.) recording spectrophotometer. Quartz cells of 1 and 0.2 cm pathlengths were used. A Beckman Model GS pH-meter with combined glass and calomel electrode was used for pH measurements.

Reagents

The stock solution of iron(III) perchlorate in 0.50 *M* perchloric acid was $1.00 \cdot 10^{-3}$ *M*. The solution contained 0.20 ml of 30% hydrogen peroxide per 100 ml to prevent the reduction of iron(III) by thiocyanate. Stock solutions of sodium thiocyanate were 0.10 *M* and 4.00 *M*. Bismuth perchlorate was $5.00 \cdot 10^{-4}$ *M* in 2.00 *M* perchloric acid; sodium iodide was 1.875 *M* in 0.0625 *M* sodium sulfite. The latter reagent was added to prevent the oxidation of iodide by air. The particular ionic strength was adjusted by addition of the corresponding amount of sodium perchlorate. The concentrations of bismuth and iron(III) were checked by titration with EDTA. Iron(III) was determined by back-titration of an excess of EDTA with a solution of thorium nitrate. Iron(III) and bismuth perchlorate were products of G. F. Smith Co., Columbus, Ohio. All other chemicals were "Bakers Analyzed Reagents".

Procedure

The sequence of metal ion and sodium thiocyanate or iodide was used in the preparation of solutions. Fresh stock solutions (prepared the same day) were used. Absorbances were measured against a thiocyanate or iodide blank. The temperature was kept at 25 ± 1°.

THEORETICAL

The absorbance of a solution containing I number of the species S_i is given by

$$A_{fg} = \sum_{1}^{I} \varepsilon_{if}[S_i]_g \tag{1}$$

where the subscripts f and g designate the wavelength of the measurement and the number of the solution, respectively; ε_{if} is the molar absorptivity of the species S_i, and $[S_i]$ is the actual concentration of that species.

If the absorbance is measured at $I+1$ different wavelengths, the concentrations of $[S_i]$ can be eliminated from the set of $I+1$ equations (1). The equation

$$\sum_{f=1}^{F-1} k_f A_{fg} + A_{Fg} = 0 \tag{2}$$

where

$$k_f = \Phi(\varepsilon_{if}) \tag{3}$$

is obtained. If the individual equations of (2) are combined for different solutions by elimination of constants k_1, k_2, ... k_{F-2}, a linear relationship is obtained:

$$k_{F-1} + k_F x + y = 0 \tag{4}$$

where

$$x = \varphi(A_{fg}) \text{ and } y = \psi(A_{fg}) \tag{5ab}$$

Equation (4) can be developed for any number of absorbing species in the solution. Any particular number of species corresponds to the particular functions of φ and ψ and can be estimated in that way.

One species is connected with $F=1$ (therefore $k_0=0$) and

$$x = A_{1a} \text{ and } y = A_{2a} \tag{6ab}$$

where $a=1, 2, 3, \ldots$ A straight line crossing the point $x=y=0$ is obtained.

Two species require $F=2$ and

$$x = A_{2a}/A_{11} \text{ and } y = A_{3a}/A_{11} \tag{7ab}$$

where $a=1, 2, 3, \ldots$

Three species correspond to $F=3$ and

$$x = (A_{1a}A_{31} - A_{11}A_{3a})/(A_{1a}A_{21} - A_{11}A_{2a}) \tag{8a}$$

$$y = (A_{1a}A_{41} - A_{11}A_{4a})/(A_{1a}A_{21} - A_{11}A_{2a}) \tag{8b}$$

where $a=2, 3, \ldots$

Four species are represented by $F=4$ and

$$x = \frac{(A_{1b}A_{21} - A_{11}A_{2b})(A_{1a}A_{41} - A_{11}A_{4a}) - (A_{1a}A_{21} - A_{11}A_{2a})(A_{1b}A_{41} - A_{11}A_{4b})}{(A_{1b}A_{21} - A_{11}A_{2b})(A_{1a}A_{31} - A_{11}A_{3a}) - (A_{1a}A_{21} - A_{11}A_{2a})(A_{1b}A_{31} - A_{11}A_{3b})} \tag{9a}$$

$$y = \frac{(A_{1b}A_{21} - A_{11}A_{2b})(A_{1a}A_{51} - A_{11}A_{5a}) - (A_{1a}A_{21} - A_{11}A_{2a})(A_{1b}A_{51} - A_{11}A_{5b})}{(A_{1b}A_{21} - A_{11}A_{2b})(A_{1a}A_{31} - A_{11}A_{3a}) - (A_{1a}A_{21} - A_{11}A_{2a})(A_{1b}A_{31} - A_{11}A_{3b})} \tag{9b}$$

where a = 2, 3, ...; b = 3, 4, ...

In this manner any number of species can be dealt with. Equations (6ab)–(9ab) are used to plot the relationship $y = \mathrm{f}(x)$ graphically. The straight line shape of the relationship indicates the corresponding number of species.

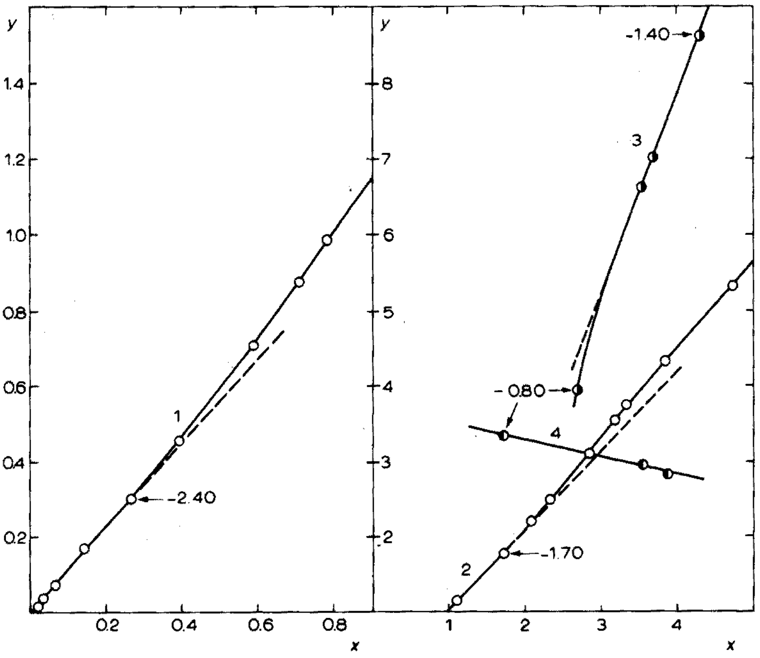
RESULTS AND DISCUSSION

Iron(III)–thiocyanate and bismuth–iodide systems

The theory developed was used for the iron(III)–thiocyanate and bismuth–iodide systems. Both systems were selected since they typically illustrate the formation of several absorbing species (complexes). The absorbances obtained are listed in Tables I and II. The determination of the number of absorbing species is presented in Figs. 1 and 2. The corresponding overall stability constants, β_n, were considered, and the percentage of the individual complexes was calculated by means of the equation

$$P_n = 100[\mathrm{ML}_n]/c_\mathrm{M} = 100\beta_n c_\mathrm{L}^n \Big/ \left(\sum_0^N \beta_n c_\mathrm{L}^n\right) \qquad (10)$$

where $\beta_0 = 1$, and c_M and c_L are the total concentrations of the metal and ligand, respectively; $[\mathrm{ML}_n]$ is the actual concentration of the complex ML_n. It was assumed that $c_\mathrm{L} \gg c_\mathrm{M}$. The dependence $P_n = \mathrm{f}(c_\mathrm{L})$ is plotted in Figs. 3 and 4. A good agreement of the results with those in Figs. 1 and 2 can be seen.



(a) (b)

Fig. 1. Dependence of $y = \mathrm{f}(x)$ for iron(III)–thiocyanate system. Numbers of absorbing species are identical with the numbers of individual curves. Limiting values of log c_SCN are given for some specific points. Other curves, that can be obtained by permutation of absorbance values, are not drawn because of clarity.

TABLE I

ABSORBANCE OF IRON(III)-THIOCYANATE SYSTEM[a]

λ(nm)	log c_{SCN}														
	−3.70	−3.40	−3.10	−2.70	−2.40	−2.10	−1.70	−1.40	−1.22	−1.10	−0.80	−0.49	−0.10	0.20	0.51
430	0.022	0.037	0.070	0.152	0.272	0.394	0.592	0.707	0.777	0.950	1.065	1.060	1.200	1.475	1.450
450	0.024	0.040	0.079	0.174	0.310	0.454	0.687	0.829	0.917	1.130	1.260	1.310	1.515	1.845	1.865
470	0.024	0.040	0.077	0.172	0.307	0.459	0.706	0.880	0.983	1.230	1.405	1.480	1.705	2.065	2.100
490	0.021	0.035	0.066	0.149	0.269	0.410	0.649	0.849	0.960	1.230	1.410	1.480	1.690	2.025	2.060
510	0.017	0.028	0.050	0.114	0.212	0.331	0.548	0.734	0.846	1.125	1.290	1.345	1.500	1.810	1.820

[a] $c_{Fe} = 2.00 \cdot 10^{-4}$ *M*; pH 1.10; ionic strength 0.20 *M* for log c_{SCN} −3.70 to −1.10, 4.00 *M* for log c_{SCN} −0.80 to 0.51.

TABLE II

ABSORBANCE OF BISMUTH–IODIDE SYSTEM[a]

λ(nm)	*log c_I*						
	−2.12	−1.82	−1.43	−1.12	−0.43	−0.12	0.18
440	0.563	0.782	0.823	0.818	0.837	1.063	1.942
460	0.473	0.726	0.912	1.052	1.290	1.360	1.587
480	0.302	0.445	0.515	0.556	0.692	0.693	0.795
500	0.168	0.192	0.173	0.146	0.146	0.146	0.176

[a] $c_{Bi} = 1.00 \cdot 10^{-4}$ *M*; 0.40 *M* perchloric acid; ionic strength 2.00 *M*.

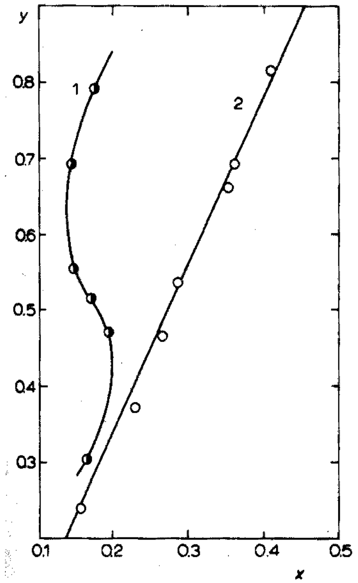


Fig. 2. Dependence of $y = f(x)$ for bismuth–iodide system. For other text see Fig. 1. Curve 1 was drawn to demonstrate that the system does not consist of one species only.

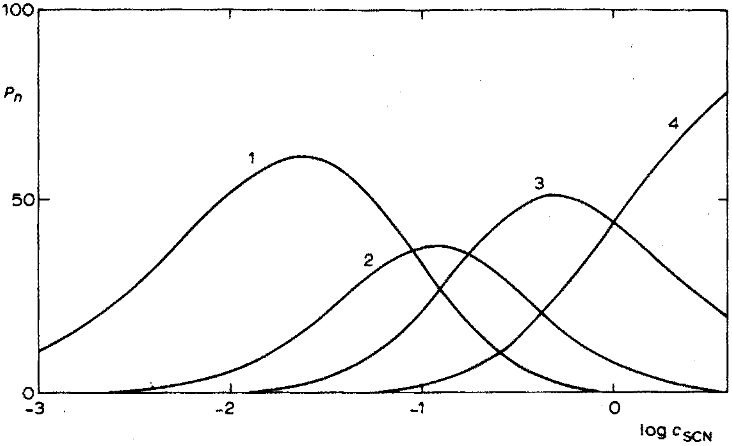


Fig. 3. Dependence of $P_n = f(\log c_{SCN})$. (1) $Fe(SCN)^{2+}$; (2) $Fe(SCN)^{+}$; (3) $Fe(SCN)_3$; (4) $Fe(SCN)_4^-$. $\beta_1 = 126$, $\beta_2 = 1380$, $\beta_3 = 7940$, $\beta_4 = 7940$ (see refs. 2 and 3). Higher complexes were not taken into account.

Absorbing metal and ligand

In a system containing metal ion and ligand, both of which absorb, the concept of effective absorbance

$$\Delta A_{fg} = \sum_{1}^{I} \Delta\varepsilon_{if} [S_i]_g \tag{11}$$

should be used instead of eqn. (1). Then:

$$\Delta A_{fg} = A_{fg} - A_{M(fg)} - A_{L(fg)} \tag{12}$$

where A_{fg} is the absorbance of the mixture, and $A_{M(fg)}$ and $A_{L(fg)}$ are the absorbances

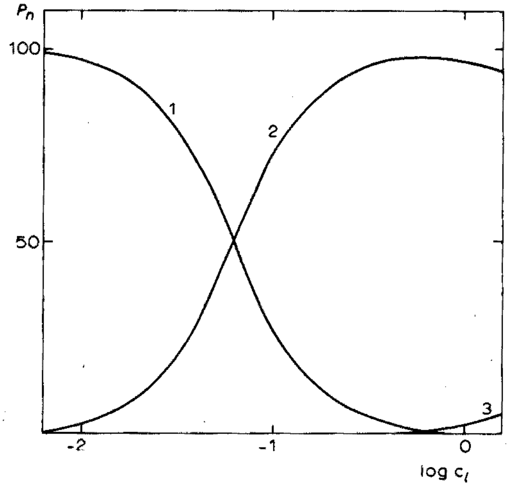


Fig. 4. Dependence of $P_n = f(\log c_l)$. (1) BiI_4^- ; (2) BiI_6^{3-} ; (3) BiI_8^{5-}. $\beta_2 = 270$, $\beta_4 = 6.48$ (BiI_4 was taken as M)[4,5].

of the metal and ligand solutions, respectively. It is assumed that the total concentrations of the metal and ligand are the same as in the mixture. The effective molar absorptivities are given by

$$\Delta\varepsilon_{if} = \varepsilon_{if} - m\varepsilon_{M(f)} - n\varepsilon_{L(f)} \qquad (13)$$

if it is assumed that a complex with molar ratio metal : ligand of $m:n$ is formed. The ε_{if}, $\varepsilon_{M(f)}$ and $\varepsilon_{L(f)}$ are the molar absorptivities of the complex (species S_i), metal and ligand, respectively.

Limits of the method

A solution of methyl red, nile blue A and brilliant green in the pH range of 4.0–6.5 is an example of a system of four absorbing species. When the methyl red–methyl orange system was investigated in the pH range 2.2–6.6, only three absorbing species were found. This result is in agreement with the findings of Wallace[6]. An apparent explanation is the similarity of the absorption spectra of the yellow forms of both dyestuffs.

The limit of applicability of the method is somewhere between three and four species because experimental error increases with the number of species. From the viewpoint of complexation this is quite sufficient since the number of consecutive complexes in a system only rarely exceeds four. However, the determination of the maximum number of species is not necessarily the objective of the method.

Conclusions

It should be pointed out that the method developed for determining the number of absorbing species in solution is a useful tool for the investigation of solutions. It is important for a subsequent investigation of the composition and stabilities of complexes, since it enables one to establish the conditions under which a minimum number of complexes is formed and in this manner to keep the system as simple as possible. Only thus can the most reliable information about the composition and stability of complexes be found.

SUMMARY

Equations for the determination of the number of absorbing species in solution were developed by a new procedure. Their use was demonstrated for the iron(III)–thiocyanate and bismuth–iodide systems. The application of the method for absorbing metals and ligands, the limits of the method and its importance for the investigation of solutions are discussed.

RÉSUMÉ

Des équations sont proposées pour la détermination d'indice d'absorption de substances en solution, en utilisant un nouveau procédé. Une application est décrite pour les systèmes fer(III)–thiocyanate et bismuth–iodure. On discute de son importance pour l'examen de solutions, et des limites de la méthode.

ZUSAMMENFASSUNG

Gleichungen für die Bestimmung der Anzahl absorbierender Spezies in Lösung wurden nach einem neuen Verfahren entwickelt und auf die Systeme Eisen(III)–Thiocyanat und Wismut–Jodid angewendet. Die Anwendung der Methode auf absorbierende Metallionen und Liganden, die Grenzen der Methode und ihre Bedeutung für die Untersuchung von Lösungen werden diskutiert.

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ANALYTICAL APPLICATIONS OF THIO-, SELENO-, AND TELLUROETHERS

PART II. SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH THIOETHERS

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In a recent study[1], a new test for the identification of palladium was developed, based on the marked extractibility of the species [$PdCl_2 \cdot 2L$] (L = thio-, seleno- and telluroethers) in benzene. On this basis, the separation of palladium chloride from solutions containing other ions was thoroughly studied and spectrophotometric measurements of the extracts were used for the determination of palladium. This study was designed, ~~like~~ the qualitative one, not only to develop a new determination of palladium, but also to show the possibility of introducing a new analytical reagent based on the reactivity of a whole class of organic substances (containing "reactive element" S, Se and Te).

The present paper describes the method based on symmetrical and asymmetrical thioethers. The reactions are sensitive and do not require close control of experimental conditions. High selectivity was obtained because thioethers can be considered as "soft bases"[2,3] owing to the presence of sulfur.

It is well known that palladium chloride forms well defined complexes with thioethers[2], hence one of the sixteen studied compounds was selected to verify the conditions for the determination of palladium, and another, benzyl sulfide, was chosen to complete the analytical study, because the benzene extract of [$PdCl_2 \cdot 2(C_6H_5-CH_2)_2S$] showed the highest molar absorptivity value. The analytical application of selenoethers is still being studied.

EXPERIMENTAL

Apparatus

A Zeiss spectrophotometer model PM QII and 1-cm silica cells were used for absorbance measurements. Absorption spectra of benzene extracts were obtained with a Cary spectrophotometer model 14. For pH measurements, a Metron potentiometer E 322 was used.

Reagents

The compounds I, II, III, IV, VII, VIII, IX, X, XI, XII, XIII (Table I) were prepared by normal methods, *i.e.*, heating alkaline solutions of thiols and the correspondent alkyl halide. Compounds V, VI, XIV, XV, XVII, XIX were obtained

TABLE I

ABSORPTION MAXIMA OF BENZENE EXTRACTS CONTAINING [$PdCl_2 \cdot 2L$]

L		*Max. (nm)*	*L*		*Max. (nm)*
I	Methyl phenyl sulfide	333	XIV	Methyl sulfide	303
II	Ethyl phenyl sulfide	325	XV	Isopropyl sulfide	310
III	n-Propyl phenyl sulfide	330	XVI	Benzyl sulfide	315
IV	Isopropyl phenyl sulfide	325	XVII	Phenyl sulfide	370
V	Methyl *p*-cresyl sulfide	345	XVIII	Benzyl selenide	341
VI	Ethyl *p*-cresyl sulfide	335	XIX	Phenyl selenide	375
VII	n-Propyl *p*-cresyl sulfide	338	XX	Phenyl telluride	400
VIII	Isopropyl *p*-cresyl sulfide	335			
IX	n-Hexyl *p*-cresyl sulfide	338			
X	Methyl *o*-cresyl sulfide	345			
XI	Ethyl *o*-cresyl sulfide	335			
XII	n-Propyl *o*-cresyl sulfide	338			
XIII	Isopropyl *o*-cresyl sulfide	335			

from Eastman Kodak. Compound XVIII was synthesized by the method of Painter *et al.*[4] and compound XX by the method of Rheinboldt and Vicentini[5]. Compound XVI was obtained either from Eastman Kodak or by synthesis[6]. Compounds XVI and XVIII were recrystallized from ethanol and the two melting points agreed with the literature data. All the others were purified by distillation under reduced pressure and their purity was verified by gas chromatography; a purity above 99.9% was always found.

Compound IX (b.p. 125°–126°; 1 mm Hg) was analysed (calculated for $C_{13}H_{20}S$: C 74.99%, H 9.60% and S 15.40%; found C 75.44%, H 9.18% and S 15.48%) as no references were found in the literature.

Benzene was distilled before use. Commercial benzene was purified by the normal method (shaken with concentrated sulfuric acid, washed with water, dried and then distilled).

All inorganic chemicals used were of analytical grade.

Standard palladium solution. This was prepared from palladium chloride to contain *ca.* 6.30 mg Pd ml^{-1} in 0.1 *M* hydrochloric acid. It was standardized gravimetrically with dimethylglyoxime.

Solutions of diverse ion. Stock solutions of different cations were prepared from their chlorides in 0.1 *M* hydrochloric acid; silver was used as its sulfate and some cations such as tin(II) and (IV), thorium(IV), zirconium(IV) and bismuth, required the addition of more concentrated acid. For the study of anions stock solutions of their sodium salts were prepared. All these contained *ca.* 10 mg of the relevant ion per ml.

Preliminary studies and spectral characteristics

For some thioethers, with a methyl or ethyl group connected to the sulfur atom, and for selenium and tellurium compounds of the group, the extraction of palladium seemed to require less time and fewer extractions for complete separation. Based on qualitative studies[1] and these additional observations, a process of 5 extractions with 1-ml portions of a 3% solution of the thioether in benzene for 5 min each time, was established as general procedure, to ensure quantitative extraction. After the extraction, all the species $[PdCl_2 \cdot 2L]$ in the benzene extracts showed absorption spectra with symmetrical and well defined maxima (Table I).

Methyl *p*-cresyl sulfide was chosen to verify quantitatively the effect of different factors such as reagent concentration, pH and chloride ion concentration in the aqueous solutions.

Effect of reagent concentration. Benzene solutions containing 3%, 1%, 0.5% and 0.1% (v/v or w/v) reagent were used to extract 11.8 μg Pd ml^{-1}, and the extracts were measured at 345 nm. Solutions containing 3% and 1% extracted easily; 0.1% required vigorous shaking 5 times with a duration of 5 min each time, and the absorbance values were slightly smaller than expected.

These results confirm preliminary observations and the proposed general procedure.

Effect of pH variations. The study of the effect of pH variations in extractions was made with perchloric acid, acetate or hydrogen phthalate buffers. The pH was varied from 1.0 to 5.7 by addition of appropriate amounts of perchloric acid or buffer. Based on absorbance values at 345 nm, quantitative separation of 11.8 μg Pd ml^{-1} could be obtained in the pH range 1.0–4.0, with 3% thioether solutions in benzene.

Effect of chloride ion concentration. Palladium chloride solutions containing 11.8 μg Pd ml^{-1} at pH 1.4 ± 0.3, and chloride concentrations varying from 0.5 *M* to 3.8 *M* (by addition of saturated sodium chloride solution), were extracted with the 3% thioether solution. The constancy of the absorbance values at 345 nm, over this chloride range, indicated that the palladium extraction was complete.

Temperature influence and color stability. Extractions done between 18° and 25° always gave a positive result, and when spectrophotometric measurements were made at 20–25° no significant discrepancy was observed.

The absorbance values of $[PdCl_2 \cdot 2\,R_2S]$ solutions in benzene, kept in the dark, were constant for three days.

Determination of palladium

It was shown that all 16 thioethers can be used to determine palladium chloride solutions at pH 1.0 when 3% solutions in benzene are used. The 16 calibration curves, plotted by employing the procedure given below, showed that Beer's Law applied in the range studied, *i.e.* 1.25–4.40 p.p.m. in the measured benzene extracts.

Benzene solutions of the thioethers showed no significant absorbance near the wavelength maximum of the corresponding $[PdCl_2 \cdot 2L]$ species; but despite this fact, all absorbance measurements were made against the respective 3% thioether solution as a blank.

Table II shows that all the thioethers were sensitive reagents for palladium, but to complete the analytical study, the most sensitive, *i.e.* benzyl sulfide, was selected.

Determination of palladium with benzyl sulfide

Spectral characteristic and calibration curve. The absorption spectrum of the complex $[PdCl_2 \cdot 2(C_6H_5CH_2)_2S]$ extracted in benzene shows a band with a well

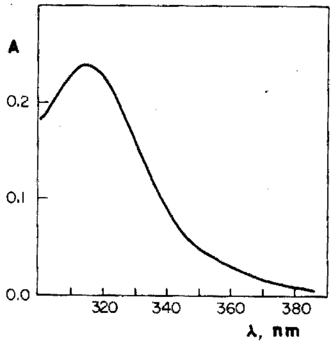

Fig. 1. Absorption spectrum of the benzene extract containing the species $[PdCl_2 \cdot 2(C_6H_5CH_2)_2S]$; 1.3 μg Pd(II) ml^{-1}.

TABLE II

MOLAR ABSORPTIVITY VALUES OF $[PdCl_2 \cdot 2L]$

L	*ε(l cm⁻¹ mol⁻¹)*	*L*	*ε(l cm⁻¹ mol⁻¹)*
Methyl phenyl sulfide	$1.43 \cdot 10^4$	Methyl *o*-cresyl sulfide	$1.35 \cdot 10^4$
Ethyl phenyl sulfide	$1.50 \cdot 10^4$	Ethyl *o*-cresyl sulfide	$1.42 \cdot 10^4$
n-Propyl phenyl sulfide	$1.54 \cdot 10^4$	n-Propyl *o*-cresyl sulfide	$1.49 \cdot 10^4$
Isopropyl phenyl sulfide	$1.54 \cdot 10^4$	Isopropyl *o*-cresyl sulfide	$1.49 \cdot 10^4$
Methyl *p*-cresyl sulfide	$1.40 \cdot 10^4$	Methyl sulfide	$1.45 \cdot 10^4$
Ethyl *p*-cresyl sulfide	$1.43 \cdot 10^4$	Isopropyl sulfide	$1.45 \cdot 10^4$
n-Propyl *p*-cresyl sulfide	$1.53 \cdot 10^4$	Benzyl sulfide	$1.93 \cdot 10^4$
Isopropyl *p*-cresyl sulfide	$1.53 \cdot 10^4$		
n-Hexyl *p*-cresyl sulfide	$1.53 \cdot 10^4$		

defined maximum at 315 nm (Fig. 1). In the measured benzene solutions the palladium complex obeys Beer's Law in the concentration range 0.63–4.40 p.p.m. According to the Ringbom method, the optimal concentration range is 1.00–3.80 p.p.m. in the final dilution.

Extraction efficiency. The extraction efficiency was estimated by extracting 1.00 ml of the aqueous solutions containing 6.30 μg or 18.9 μg of palladium, with 1.0 ml of a 3% benzyl sulfide solution in benzene. It was found that 65% of the palladium was extracted in a single pass at each of the two concentrations.

Study of interferences

The previous qualitative results[1] indicated that quantitative separation and determination of palladium should be possible even in the presence of other platinum group ions, other metallic ions, and many different anions.

Special attention was given to the determination of palladium in the presence of platinum, as it was observed that this metal interfered mainly when thioethers containing methyl or ethyl radicals bound to the sulfur atom were used. Benzyl sulfide extracted a certain amount of some platinum species, giving some absorbance in the region of the palladium complex maximum. This interference was easily eliminated by addition of some aqueous iron(III) solution; iron(III) probably inhibits a reaction between thioethers and platinum. Different concentrations of platinum and iron(III), and different thioethers were studied, resulting in the expected inhibition. Only methyl phenyl sulfide gave a small absorbance value.

If ethyl *p*-cresyl sulfide is utilized to determine palladium in the presence of platinum with iron(III) as inhibitor, the extraction should be as rapid as possible; otherwise, there is some interaction between iron(III) and the thioether, resulting in a red extract (absorption spectrum with maximum at 460 nm), which interferes in the determination.

Gold, and some anionic interferences such as bromide, iodide, azide, thiocyanate, oxalate, sulfide, thiosulfate and nitrite were easily eliminated, the first with ascorbic acid and the others with aqua regia.

Table III gives the data for the determination of palladium in the presence of diverse ions.

Precision

The precision of the method involving separation and spectrophotometric determination of palladium in the presence of the foreign ions studied, was evaluated from 70 runs: 35 with aqueous solutions containing 6.3 μg Pd ml^{-1} with variable amounts of foreign ions, and another 35 with 18.9 μg Pd ml^{-1}.

For the first set the standard deviation calculated from the absorbances obtained, was 0.005 and the probable error for a single measurement was 0.003. This means that a single determination should be correct within ±0.08 μg of palladium. For the second set, the standard deviation was 0.008 and the probable error 0.006; thus a single determination should be correct within ±0.16 μg of palladium.

Recommended procedures

Separation and determination of palladium. To 1.00 ml of the test solution, which should be about 0.1 *M* in hydrochloric acid, in a ground-glass-stoppered test tube (*ca.* 10 ml), add a drop of iron(III) chloride solution (also 0.1 *M* in hydrochloric acid and containing *ca.* 500 μg per drop). Agitate vigorously for 5 min with 1.0 ml of a 3% solution of the thioether in benzene. Centrifuge to separate the phases and remove the organic layer, transferring to a 5.0-ml volumetric flask with an extraction pipette[7]. Repeat the extraction four times with 1.0 ml each time, transferring all the extracts to the 5.0-ml flask. Read the absorbance at the maximum (benzyl sulfide, 315 nm), against a blank run in parallel with all the reagents present.

Determination of palladium in the presence of gold. Agitate vigorously 1.00 ml of the test solution (Pd(II) and Au(III)) which should be about 0.1 *M* in hydrochloric acid, with 1.0 ml of 3% solution of benzyl sulfide in benzene for 5 min. Run a parallel blank containing the same amount of gold(III). Then add 4 drops of aqueous 2% ascorbic acid solution to each extraction tube, and shake vigorously for 20–30 min. The yellow extract (gold complex) in the blank is completely decolorized, whereas the normal yellow color remains in the sample tube. After this, follow the above procedure, and read the absorbance against the blank.

Determination of palladium in the presence of bromide, iodide, azide, thiocyanate, thiosulfate, sulfite, oxalate and nitrite. Place two extraction tubes containing the test

TABLE III

DETERMINATION OF PALLADIUM IN PRESENCE OF DIVERSE IONS

Diverse ion	*(µg)*	*Pd present (µg)*	*Pd found (µg)*	*Diverse ions*	*(µg)*	*Pd present (µg)*	*Pd found (µg)*
Pt(IV)	1000	6.30	6.25, 6.27	Ag(I)	1000	6.30	6.27, 6.25
Fe(III)	500	18.9	19.0, 18.7	Fe(III)	500	18.9	19.0, 18.8
Pt(IV)	2000	6.30	6.25, 6.30	Tl(I)	1000	6.30	6.30, 6.27
Fe(III)	500	18.9	18.7, 18.8	Fe(III)	500	18.9	18.6, 18.6
Rh(III)	1000	6.30	6.46, 6.30	Bi(III)	1000	6.30	6.30, 6.46
Ir(IV)	1000			V(III)	1000		
Fe(III)	500	18.9	19.1, 18.7	Fe(III)	500	18.9	19.0, 18.6
Ru(IV)	1000	6.30	6.25, 6.30	Pb(III)	1000	6.30	6.13, 6.07
Fe(III)	500	18.9	18.6, 18.6	Sn(IV)	1000		
				Th(IV)	1000		
Ni(II)	1000	6.30	6.32, 5.96	Zr(IV)	1000	18.9	19.0, 18.8
Co(II)	1000			Fe(III)	500		
Fe(III)	500	18.9	19.1, 19.1				
				Au(III)	1000	6.30	6.57, 6.57
Zn(II)	1000	6.30	6.41, 6.63	HPO_4^{2-}	1000	6.30	6.18, 6.30
Cd(II)	1000			$HAsO_4^{2-}$	1000		
Hg(II)	1000	18.9	19.4, 19.4	NO_3^-	1000	18.9	19.1, 19.3
Fe(III)	500			Fe(III)	1000		
Cr(III)	1000	6.30	6.13, 6.07	ClO_4^-	1000	6.30	6.32, 6.46
Mn(II)	1000			SO_4^{2-}	1000		
UO_2(II)	1000	18.9	18.6, 19.0	VO_3^{2-}	1000	18.9	19.1, 18.8
Fe(III)	500			Fe(III)	500		
Al(III)	1000	6.30	6.32, 6.41	MoO_4^{2-}	1000	6.30	6.32, 6.30
In(III)	1000			WoO_4^{2-}	1000	18.9	18.8, 18.8
Ga(III)	1000			Br^-	1000	6.30	6.25, 6.13
Be(II)	1000	18.9	19.0, 19.0	I^-	1000	18.9	18.6, 18.6
Fe(III)	500			N_3^-	1000	6.30	6.25, 6.18
				SCN^-	1000	18.9	19.0, 18.8
Cu(III)	1000	6.30	6.27, 6.18	S^{2-}	1000	6.30	6.30, 6.32
Fe(III)	500	18.9	19.1, 18.8	SO_3^{2-}	1000	18.9	19.0, 18.8

solution and the blank in an adequate support, slightly tilted, and evaporate the solutions under an infra-red bulb (this treatment eliminates many anions, as they are incompatible with acid medium). Add 5 drops of concentrated nitric acid and evaporate gently, repeat this process, then add 5 drops of concentrated nitric acid and 15 drops of concentrated hydrochloric acid, and eliminate the nitric acid. Complete the elimination by addition and evaporation of 1.0 ml of 0.1 *M* hydrochloric acid. Then add 1.00 ml of 0.1 *M* hydrochloric acid to each tube and apply the above general procedure.

Extracted palladium complex

The palladium complex $[PdCl_2 \cdot 2(C_6H_5CH_2S)_2]$ was prepared and identified by Mann and Purdie[8]. When their procedure was used, the same substance was obtained. The absorption spectra of benzene solutions of the compound isolated, and of the extracts prepared by the recommended procedure, were identical. The absorption spectrum in the far infra-red showed the characteristic Pd–S and Pd–Cl bands[9].

DISCUSSION

In recent years, numerous colorimetric methods, with or without solvent extraction, have been proposed for palladium[10–12]. Beamish[10] recommends, however, that the probable presence, after the sample dissolution process and solution preparation, of "associated" metals (*e.g.* Ni, Cu, Fe, Pb, Au, Ag, Cr) and anions (*e.g.* nitrate, chloride, bromide, sulfate and perchlorate) should not be forgotten. Many analytical methods will have their merits minimized if these potential interferences are not considered. Accordingly, in the development of the analytical method proposed here, special attention was given to platinum interference.

When the uncharged thio, seleno and telluroether reagents are used, the pH dependence of the reactions is restricted to the species in aqueous solutions, hence the method will have fewer variables than others based on pH-dependent reagents.

The selectivity of the proposed method was partly predicted from the results of Livingstone[2], on the behavior of thioethers with metallic ions. Livingstone considered different factors in the complexing ability of ligands containing sulfur, selenium and tellurium as donor atoms. Based on electrostatic and covalent models, the complexing capacity for uncharged ligands should follow the order $R_2O > R_2S > R_2Se > R_2Te$. Thus the covalent model is developed by taking into account contributions of π-bonding. Sulfur has vacant d orbitals which can receive d electrons from some transition metals forming d_π–d_π bonding. The extent to which such bonding occurs with ligands containing sulfur, is not completely known, but some evidence suggests that it is less than for R_3P, R_3As, CN^- and CO ligands[2]. Such π-bonding conditions are more propitious with certain transition metals in their normal oxidation states (Pd(II), Pt(II), Hg(II), Au(III)) and some transition metals in low oxidation states.

Bark and Brandon[13] confirmed these suppositions, and proposed for palladium(II) the following stability order for complex formation: $O < S \geqslant Se > Te$. The ideas of Ahrland *et al.*[14] and Pearson[3] on the behavior of metal ions and ligands are well known. Divalent sulfur, selenium and tellurium in organic molecules confer the properties of "soft bases" and therefore are strongly bound to "soft acids", as in the case of some transition metals. Pearson[3] also considered the ability of "soft acids" to convey d and p electrons to "soft bases", thus forming π-bonds. Thus the formation constants of complexes containing heavy halides and sulfur compounds as ligands are high, when the complexes have low-spin d^8 ions (*e.g.* Pd(II), Pt(II), Au(III)) and d^{10} ions (*e.g.* Cu(I), Hg(II), Ag(I) and Au(I))[2]. Basolo and Pearson[15] pointed out that although there is little data on substitution reaction of palladium complexes, there is sufficient to conclude that they are typical plane-quadratic substitutions, and that the formation of palladium(II) systems is 10^5 more rapid than the corresponding platinum(II) systems. Therefore highly selective reagents for palladium(II), *viz.* thio, seleno and telluroethers, should be possible. The experimental results described here confirm this selectivity, which is enhanced by the extraction techniques.

Platinum(IV) is a moderately "hard Lewis acid", *i.e.* it does not have a strong affinity for thioethers[2], yet colored extracts were obtained, when some thioethers reacted with platinum(IV)[1]. These reactions are strongly photosensitive. Replacement reactions involving haloplatinate(IV) anions, which are not only catalyzed by thiosulfate, iron(II) and iodide, but strongly photosensitive, have been reported[16–27], but the substitution mechanism has not been discussed in detail.

From an analytical point of view, platinum(VI) may interfere by exchange reactions catalyzed by the above-mentioned ions or by daylight. As these catalytic ions are one-electron reductants, it seemed worthwhile to use a one-electron oxidant to avoid the interactions between thioethers and platinum(IV). Obviously the ion chosen should not react with palladium or thioethers. The "hard Lewis acid" iron(III) was selected. Preliminary studies were made with variable amounts of iron(III) and other oxidants, but no conclusions were reached about the inhibitive mechanism.

The effect of light was studied by running parallel extractions in daylight and diffused light, and a marked difference in absorbance values was observed.

The actual reaction mechanism (reaction and extraction) requires cautious consideration

$$[PdCl_4]^{2-}_{(aq)} + L_o \rightleftharpoons [PdCl_2 \cdot 2L]_o + 2\,Cl^-_{(aq)}$$

About $[PdCl_4]^{2-}_{(aq)}$, Wyatt[28] pointed out that this species could, in aqueous solutions, suffer aquation, hydrolysis and polymerization, depending on pH variations. In the pH range 1–3, the absorption spectrum of palladium chloride solutions does not change, and has a characteristic band at 23000 cm^{-1}. Another interesting fact[28] is that as the pH increases above 3 (partial hydrolysis and aquation) polymerization occurs, which increases with ageing of the solutions.

If it is assumed that the reactions occur between monomers and thioethers, then with pH increase and ageing solutions, the monomer would polymerize, inhibiting the complex formation. The following experimental facts were observed: above pH 4.0 with aged solutions, it was impossible to extract palladium chloride.

Further studies are necessary to clarify the position of thioethers in the spectrochemical series[2]. However, the following observations may assist in future considerations.

Benzene solutions of $[PdCl_2 \cdot 2L]$ show the wavelength of maximum absorbance shifted to the visible region, compared to $[PdCl_4]^{2-}$. The complexes formed between palladium chloride and asymmetrical thioethers with the methyl group attached to a sulfur atom showed maxima nearer the visible region than others that contained ethyl, n-propyl and isopropyl groups. Complexes containing the ethyl group bound to the sulfur had the same maxima as those containing an isopropyl group. The introduction of a methyl group into the benzene ring, in the *ortho* or *para* position produced absorption maximum shifts of *ca.* 10 nm.

The results obtained indicate that compounds R–E–R are highly selective in the case of palladium(II), and that the elements, E = S, Se and Te could be considered as "reactive elements" for this ion.

Versatility was also reached as all the thioethers studied may be used for detection or determination of palladium; the proposed methods are simple and do not require strict experimental controls.

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SUMMARY

Palladium is very efficiently extracted with benzene solutions of thio, seleno and telluroethers from acidic solutions. Methods based on symmetrical and asymmetrical thioethers are presented. Benzene solutions of 16 thioethers can be used to determine palladium spectrophotometrically in the range 1.25–4.40 p.p.m. in the measured extracts. Separation of palladium from platinum metals, as well as many other metal ions and anions is reported.

RÉSUMÉ

On décrit une méthode spectrophotométrique pour le dosage du palladium. On procède par extraction à l'aide de solutions benzéniques de thio-, séléno- et telluroéthers (1.25 à 4.40 p.p.m. Pd dans extrats). On propose une méthode de séparation du palladium d'avec les métaux du platine ainsi que d'avec de nombreux autres ions métalliques et anions.

ZUSAMMENFASSUNG

Palladium wird aus sauren Lösungen sehr wirksam mit benzolischen Lösungen voh Thio-, Seleno- und Telluroäthern extrahiert. Bei den vorgelegten Methoden werden symmetrische und asymmetrische Thioäther verwendet. Benzolische Lösungen von 16 Thioäthern eignen sich für die spektrophotometrische Bestimmung von Palladium bei einer Konzentration von 1.25–4.40 p.p.m. im Extrakt. Palladium lässt sich von Platinmetallen und auch von vielen anderen Metallionen und Anionen abtrennen.

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THE OXIDATION OF HYDROXYLAMINE WITH COBALT(III)

A STUDY OF VARIABLE REACTION STOICHIOMETRY

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The oxidation of hydroxylamine with excess of cobalt(III) has already been described in a previous paper[1]. It was found that the reaction is catalyzed by cobalt(II), and a probable mechanism of this catalysis was proposed. Catalysis by cobalt(II) ions was also observed in the oxidation of hydrazine[2], for which the same catalytic mechanism applied as for the hydroxylamine oxidation.

In the previous study of the hydroxylamine oxidation[1], it was assumed, on the basis of titrations of hydroxylamine with a cobalt(III) solution, that the oxidation proceeded with exchange of four electrons, *i.e.* with formation of nitrite. Only very approximate information about the stoichiometry in the presence of excess of cobalt(III) could be found by determining the cobalt(III) concentration from its spectra, since there was always additional reduction of cobalt(III) by water.

Since the oxidation of nitrite with cobalt(III) has been studied in a recent paper[3], the oxidation of hydroxylamine was re-investigated. A mixing adaptor was constructed for the Unicam SP800 spectrophotometer, which allowed faster reactions to be followed, so that the hydroxylamine oxidation could be followed up to a twenty-fold excess of hydroxylamine, where the oxidation proceeds quantitatively to nitrogen. The present investigations made possible the solution of the overall mechanism of the multistep oxidation.

EXPERIMENTAL

The cobalt(III) perchlorate solutions were prepared and standardized as described previously[1]. The hydroxyammonium sulphate solution was also obtained as described previously[1].

Potentiometric titrations were performed with a Multoscop V potentiometer (Laboratorní přístroje, Czechoslovakia), with a platinum indicator and a saturated calomel reference electrode.

Kinetic measurements of the cobalt(III) reaction with hydroxylamine in the presence of excess of cobalt(III) were made on a Unicam SP800 spectrophotometer with 1-cm cuvettes[2]. The time dependences of the absorbance at a constant wavelength were recorded with an external recorder (EZ-2 electronic recorder, Laboratorní

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přístroje, Czechoslovakia) with a maximum chart speed of 180 mm min^{-1}, and a pen response rate of 3 s for f.s.d. All solutions were thermostatted at 25°.

In order to find the reaction order with respect to cobalt(III) and hydroxylamine, measurements were carried out at various equivalent concentrations of the two reactants, and at a small excess of cobalt(III) ($[\mathrm{Co(III)}]=1\cdot 10^{-3}$, $[\mathrm{NH_2OH}]=0.17\text{–}1\cdot 10^{-3}$ *M*) in a medium of 5 *M* perchloric acid, with an initial cobalt(II) concentration of $5\cdot 10^{-3}$ *M*. The dependence of the reaction rate on the cobalt(II) concentration was further measured in 5 *M* perchloric acid medium. The dependence of the reaction rate on the hydrogen ion concentration was followed in media 2–5 *M* in perchloric acid, at ionic strength, $\mu=5$, maintained with sodium perchlorate.

The kinetic measurements of the hydroxylamine oxidation, when this reagent was in excess, were also carried out spectrophotometrically, but, when faster reaction rates were studied, a specially designed mixing adapter to the Unicam SP800 spectrophotometer was used (Fig. 1). This adapter differs from conventional devices in its simplicity and, primarily, in the possibility of using normal spectrophotometric cuvettes (*i.e.*, flow-through cuvettes are unnecessary). The adapter is all-glass and can therefore be used even with strong acids. The first concentration reading could be taken at the time, $t=1$ s, which practically corresponds to the response rate of the recorder. Even if the actual mixing of solutions takes a certain time, this time is very short and is negligible compared to the response time of the recorder and to the overall reaction time.

The principle of the adapter is as follows: through a specially made opening in the spectrophotometer cover, the adapter is connected with the cuvette by means of the ground-glass joint, Z, and is evacuated through the tube at the stopcock, K_2. On opening the two-way stopcock, K_1, both solutions enter the cuvette from their

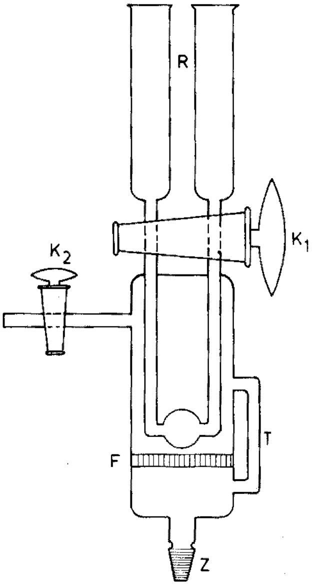


Fig. 1. The mixing adapter for the Unicam SP800 spectrophotometer, (R) Reservoir; (K_1 and K_2) stopcocks with ground-glass joints; (F) sintered glass filter; (T) tube, (Z) ground-glass joint with the cuvette.

reservoirs under atmospheric pressure, being mixed in the cylinder before the cuvette. The sintered glass filter prevents formation of bubbles in the solution entering the cuvette and ensures perfect mixing of the solutions. The tube, T, serves for rapid pressure balancing. Evacuation not only helps, by applying atmospheric pressure, with fast mixing of solutions, but also prevents formation of air bubble blocks.

The absorbance of the solutions in dependence on time was measured at a constant wavelength, by means of the external recorder. The function and applicability of the adapter were tested by mixing solutions with known concentrations of cobalt(III) with the same volume of 5 M perchloric acid (5 ml). The absorbances of these solutions were compared with those of cobalt(III) solutions of the same concentrations, measured without the use of the adapter. The absorbances of corresponding solutions were identical, within experimental error, with a reproducibility of 2%, 1 s after opening the stopcock, K_1.

The reaction order with respect to cobalt(III) and hydroxylamine, for the reaction in the presence of excess of hydroxylamine, was found by measurements at 1–20-fold excesses of hydroxylamine ($[\mathrm{Co(III)}] = 1 \cdot 10^{-3}$ M) in 5 M perchloric acid medium. The reaction rate dependence on the cobalt(II) concentration was determined in the same medium. The rate dependence on $[H^+]$ was followed within the range 2–5 M perchloric acid, in a medium with the ionic strength, $\mu = 5$, maintained with sodium perchlorate.

The stoichiometry of the cobalt(III) reaction with hydroxylamine was found from the spectra after completion of the reaction in the case of the oxidation in the presence of excess of cobalt (III); for equivalent concentrations of cobalt(III) and hydroxylamine, and a small excess of hydroxylamine, the stoichiometry was derived from the course of the *c–t* dependences and from the other kinetic data. The reaction stoichiometry in the presence of 4–15-fold excesses of hydroxylamine was determined by an indirect titration of the unreacted excess with a 0.01 M iodine monochloride solution in 3 M perchloric acid, which was back-titrated with a 0.05 M hydroxyammonium sulphate solution[4].

RESULTS

The oxidation to nitrate

When initial concentrations of 0.83–3.3 $\cdot 10^{-4}$ M hydroxylamine and 0.5–2 $\cdot 10^{-3}$ M cobalt(III) were used, it was found from the spectra that, in the presence of a 6-fold excess of cobalt(III), a six-electron oxidation of hydroxylamine proceeded according to the overall equation:

$$6\,\mathrm{Co(III)} + \mathrm{NH_2OH} + 2\,\mathrm{H_2O} \rightarrow 6\,\mathrm{Co(II)} + \mathrm{NO_3^-} + 7\,\mathrm{H^+}$$

In order to distinguish between the cobalt(III) reactions with hydroxylamine and with water, the straight lines of $\log[\mathrm{Co(III)}]$ against time were plotted. In the case of higher cobalt(III) excesses, breaks occurred on these straight lines after the completion of the reaction with six equivalents of cobalt(III), since the cobalt(III) reaction with water was slower, even if not substantially so, than that with hydroxylamine. The water oxidation proceeded faster in this case than in that observed previously[1], probably because it was catalyzed by the nitrate ions formed. The small difference in the rates of both the reactions evidently caused the previous erroneous stoichiometry determination[1].

To verify the reaction products, a qualitative test for nitrates with brucine[5] was carried out, which was positive in all the above experiments. To detect nitrites, the coupling reaction with sulphanilic acid and α-naphthylamine[5] was carried out. Nitrite was not detected in any reaction mixture, even after reaction in the presence of a smaller excess of cobalt(III) ($[\mathrm{Co(III)}] = 1 \cdot 10^{-3}$ *M*; $[\mathrm{NH_2OH}] \approx 0.17\text{–}1 \cdot 10^{-3}$ *M*), although the cobalt(III) consumption decreased with decreasing excess of cobalt(III), as was found from the kinetic measurements given below.

A first-order rate equation applied for the reaction of equivalent concentrations of cobalt(III) and hydroxylamine, and also at a small excess of hydroxylamine. By plotting log[Co(III)] against time, straight lines were obtained for initial concentrations of $\mathrm{Co(III)} = 1 \cdot 10^{-3}$ *M* and of hydroxylamine $\approx 0.17\text{–}1 \cdot 10^{-3}$ *M*, similarly as in the previous paper[1]. The first-order straight lines applied also for measurement at equivalent cobalt(III) and hydroxylamine concentrations ($[\mathrm{Co(III)}] \approx 0.5\text{–}2 \cdot 10^{-3}$ *M*, $[\mathrm{NH_2OH}] \approx 0.083\text{–}0.33 \cdot 10^{-3}$ *M*).

From the results given it is obvious that the reaction is first order with respect to cobalt(III), and at the given initial concentration of hydroxylamine is zero order with respect to this reagent. The first-order rate constant, *k*, was evaluated graphically from the above relationships, for which it holds that $k = -\mathrm{tg}\alpha \cdot 2.303$. The constant, *k*, was always evaluated from four replicate measurements, the reproducibility of which was 2–3% (Table I). For equivalent cobalt(III) and hydroxylamine concentrations, the constant *k* increased linearly with increasing hydroxylamine concentration, but the straight line did not pass through the origin (Fig. 2). On plotting *k* against the initial concentration of hydroxylamine, which was present at a small excess, a curve was obtained instead of the expected straight line (Fig. 3); for a hydroxylamine concentration of $1 \cdot 10^{-3}$ *M*, only 5 equivalents of cobalt(III) reacted with one equivalent of hydroxylamine. It is obvious from the relation for the rate, $v = -d[\mathrm{Co(III)}]/\mathrm{d}t = -n\mathrm{d}[\mathrm{NH_2OH}]/\mathrm{d}t = nk'[\mathrm{Co(III)}][\mathrm{NH_2OH}]$, that the rate and therefore also the constant, k ($k = nk'[\mathrm{Co(III)}]$) will decrease by 1/6 of its value with a decrease in the cobalt(III) consumption to 5 equivalents. This decrease resulted in the previous conclusion[1] that the rate of the oxidation is independent of the hydroxylamine concentration.

TABLE I

THE FIRST-ORDER RATE CONSTANTS FOR THE COBALT(III) REACTION WITH HYDROXYLAMINE

(5 *M* $\mathrm{HClO_4}$, $[\mathrm{Co(II)}] = 5 \cdot 10^{-3}$ *M*)

10^3 [*Co(III)*] (*M*)	10^3 [NH_2OH] (*M*)	10^3 k (s^{-1})
0.5	0.083	1.92 ± 0.04
1	0.17	2.69 ± 0.07
1.5	0.25	3.68 ± 0.09
2	0.33	4.38 ± 0.13
1	0.25	3.72 ± 0.09
1	0.5	6.31 ± 0.16
1	1	10.10 ± 0.28

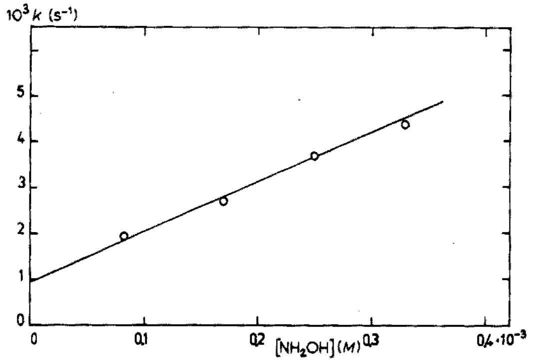
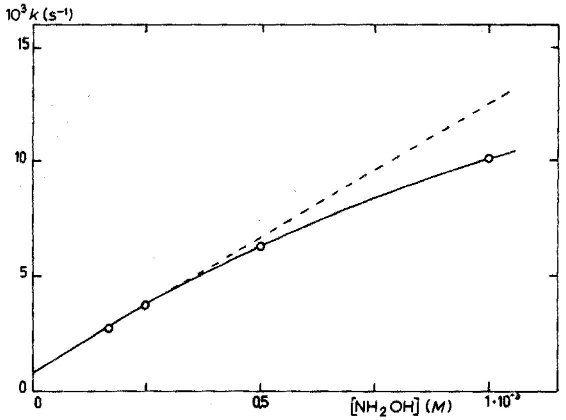


Fig. 2. The dependence of the rate of the cobalt(III) reaction on the initial concentration of hydroxylamine. 5 *M* $HClO_4$, equivalent concentrations of Co(III) and NH_2OH, $[Co(II)] = 5 \cdot 10^{-3}$ *M*.



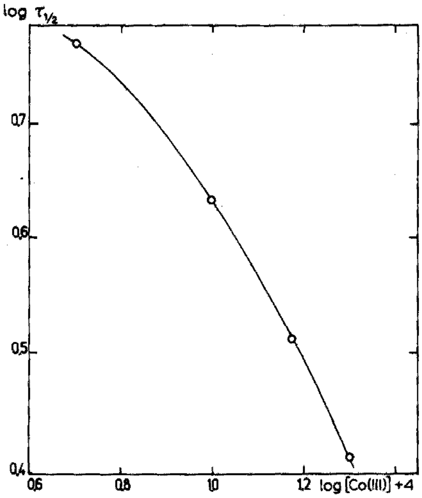


Fig. 3. The dependence of the rate of the cobalt(III) reaction on small excesses of hydroxylamine. 5 *M* $HClO_4$, $[Co(III)] = 1 \cdot 10^{-3}$ *M*, $[Co(II)] = 5 \cdot 10^{-3}$ *M*.

Fig. 4. The determination of the overall order of the cobalt(III) reaction with hydroxylamine from the half-times. 5 *M* $HClO_4$, $[Co(II)] = 5 \cdot 10^{-3}$ *M*.

As can be seen, the reaction is generally not zero order with respect to hydroxylamine, but its course is complicated. For this reason, an attempt was made to determine the overall reaction order from half-times. For equivalent initial cobalt(III) and hydroxylamine concentrations, the relationship $\log \tau_{\frac{1}{2}} = \log \text{const} - (n-1) \log a$ is valid, where a is the initial concentration of the reactants ($a = [Co(III)] = 6[NH_2OH]$), $\tau_{\frac{1}{2}}$ is the time required for the reaction of one half of a, and n is the overall reaction order. On plotting $\log \tau_{\frac{1}{2}}$ against $\log a$, a straight line with slope equal to $(1-n)$ should be obtained for constant reaction order. Since a curve was obtained (Fig. 4), it is obvious that the overall reaction order changes. The orders, calculated from Fig. 4 for various concentration regions, together with corresponding half-times, are summarized in Table II. Since the order with respect to cobalt(III) was

TABLE II

THE OVERALL REACTION ORDER OF THE COBALT(III) REACTION WITH HYDROXYLAMINE, OBTAINED FROM THE HALF-TIMES

(5 M $HClO_4$, [Co(II)] = $5 \cdot 10^{-3}$ M)

10^3 [*Co(III)*] (M)	0.5	1.0	1.5	2.0
$\tau_{\frac{1}{2}}$ (min)	5.9	4.3	3.25	2.57
n	1.46	1.69	1.82	—

unity in all cases, the order with respect to hydroxylamine, (in the range $0.83–3.3 \cdot 10^{-4}$ M) increased from 0.46 to 0.82 with increasing hydroxylamine concentration.

Because of the complexity of the reaction, an attempt was made to evaluate the reaction orders with the help of a computer. From the integral c–t curves, instantaneous rates were obtained by fitting corresponding curves to known analytical functions and by their direct derivation. The most suitable were linear regressions of a third-order polynomial or a hyperbolic tangential function. The initial rates were evaluated only from regressions of a parabola because of the inflection of the hyperbolic tangential function at $x = 0$. The computation was carried out with the Minsk computer.

From rates obtained in this way for various times, the reaction orders were computed by the empirical equation $v = k\, c_A^{\alpha} c_B^{\beta} \ldots$ The equation was linearized by means of natural logarithms and the reaction orders were computed by the least squares method, with an IBM 7040 computer.

However, for the cobalt(III) reaction with hydroxylamine, an integral order with respect to hydroxylamine was not found; the order was generally higher than 2, which lacks any physical meaning. These errors were apparently caused by the application of the experimental data and by the varying reaction stoichiometry. Good results were obtained in determinations of the order with respect to cobalt(III), which was found to be unity in all cases.

It was found that at a certain initial concentration of hydroxylamine, the reaction had overall first order, and this fact was utilized in determining the reaction rate dependence on the cobalt(II) and hydrogen ion concentrations. The initial concentrations of the components were: [Co(III)] = $1 \cdot 10^{-3}$, [NH_2OH] = $0.17 \cdot 10^{-3}$ M. The dependence on the cobalt(II) concentration was measured within the [Co(II)] region, 0.005–0.1 M. The first-order rate constants were evaluated graphically; the reproducibility of repeated measurements was 3–4% (Table III). The constant k

TABLE III

THE DEPENDENCE OF THE RATE OF THE COBALT(III) REACTION WITH HYDROXYLAMINE ON [Co(II)]

(5 M $HClO_4$, [Co(III)] = $1 \cdot 10^{-3}$ M, [NH_2OH] = $0.17 \cdot 10^{-3}$ M)

[Co(II)] (M)	0.01	0.03	0.05	0.07	0.1
$10^3\,k$ (s^{-1})	3.23	4.68	6.51	8.10	10.52
Error (s^{-1})	±0.11	±0.18	±0.21	±0.31	±0.42

increased linearly with increasing cobalt(II) concentration, in the same way as had been observed previously[1] for a slightly higher concentration of hydroxylamine.

The dependence on $[H^+]$ was measured at $\mu=5$, within the range, 2–5 *M* perchloric acid (initial $[Co(II)]=5\cdot10^{-3}$ *M*). The constant, *k*, again evaluated graphically, only slightly increased with increasing hydrogen ion concentration (Table IV). This increase was probably due to maintenance of the ionic strength with sodium perchlorate, since sodium ions are not quite equivalent to the hydrogen ions which they replace. The dependence of the rate on the perchloric acid concentration was previously found to be linear without maintenance of constant ionic strength[1], hence it is evident that the reaction rate increases with increasing ionic strength.

TABLE IV

THE DEPENDENCE OF THE RATE OF THE COBALT(III) REACTION WITH HYDROXYLAMINE ON $[H^+]$

($\mu=5$, $[Co(III)]=1\cdot10^{-3}$ *M*, $[NH_2OH]=0.17\cdot10^{-3}$ *M*, $[Co(II)]=5\cdot10^{-3}$ *M*)

$[H^+]$ (*M*)	5	4	3	2
$10^3\,k$ (s^{-1})[a]	2.69	2.68	2.45	2.11

[a] Average error, 0.08 s^{-1}.

Oxidation in the presence of excess of hydroxylamine

In the presence of excess of hydroxylamine, the cobalt(III) consumption decreased to a limiting value (for a 4–6-fold excess), which corresponded to the consumption of one equivalent of cobalt(III) per equivalent of hydroxylamine. Jijie and Santappa[6] oxidized hydrozylamine in a nitric acid–sulphuric acid medium and found the same stoichiometry, *i.e.* 1:1.

In the presence of 1–3-fold excess of hydroxylamine ($1\cdot10^{-3}$ *M* Co(III), $1\text{–}3\cdot10^{-3}$ *M* NH_2OH), the reaction showed variable stoichiometry and proceeded with the consumption of 2–5 equivalents of cobalt(III), as was proved by the kinetic measurements given below. The results for the stoichiometry at 4–15-fold excess of hydroxylamine are summarized in Table V. A colourless gas, probably nitrogen, was the product of the reaction; with a 4-fold excess of hydroxylamine, nitrate was also a product. A perceptibly smaller amount of nitrogen was formed from a 4-fold excess of hydroxylamine than from a 10-fold excess.

The dependence of [Co(III)] on time was S-shaped, at cobalt(III) and hydroxylamine concentrations of $1\cdot10^{-3}$ *M* and $1\text{–}3\cdot10^{-3}$ *M*, respectively, caused

TABLE V

THE STOICHIOMETRY OF THE COBALT(III) REACTION WITH EXCESS OF HYDROXYLAMINE

(5 *M* $HClO_4$; initial Co(III) concentration, $1\cdot10^{-3}$ *M* and $2\cdot10^{-3}$ *M*)

$[NH_2OH]_0/[Co(III)]_0$	4	6	8	10	15
$\Delta[Co(III)]/\Delta[NH_2OH]$	1.5	1.2	1	1	1

by the varying reaction stoichiometry. The reaction proceeding with a consumption of six equivalents of cobalt(III) had a rate, expressed by the [Co(III)] decrease, six times higher than that of the reaction with consumption of one equivalent of cobalt(III), as follows from the rate equation: $v = -\mathrm{d}[\mathrm{Co(III)}]/\mathrm{d}t = -n\mathrm{d}[\mathrm{NH_2OH}]/\mathrm{d}t = nk'[\mathrm{Co(III)}][\mathrm{NH_2OH}]$.

In measurements with a 6–20-fold excess of hydroxylamine the order with respect to cobalt(III) was unity. On plotting log[Co(III)] against time, straight lines of pseudofirst order were obtained for cobalt(III) and cobalt(II) initial concentrations of $1\cdot10^{-3}$ *M* and $5\cdot10^{-3}$ *M*, respectively. On evaluating the reaction kinetics with a computer, first order with respect to cobalt(III) was also found; the computations were carried out in the same way as for the oxidation of hydroxylamine to nitrate.

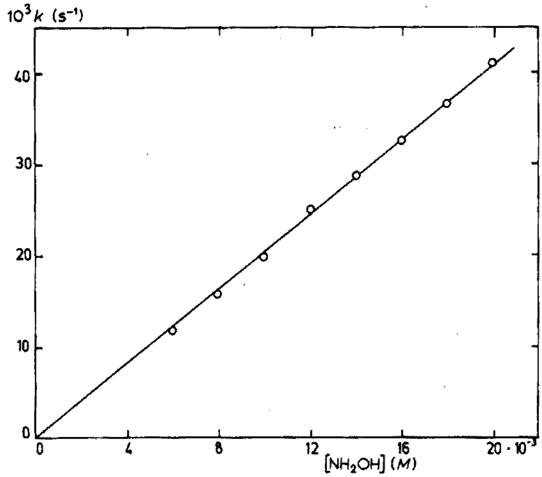


Fig. 5. The dependence of the rate of the cobalt(III) reaction with hydroxylamine on the initial hydroxylamine concentration. 5 *M* $\mathrm{HClO_4}$, [Co(III)] $= 1\cdot10^{-3}$ *M*, [Co(II)] $= 5\cdot10^{-3}$ *M*.

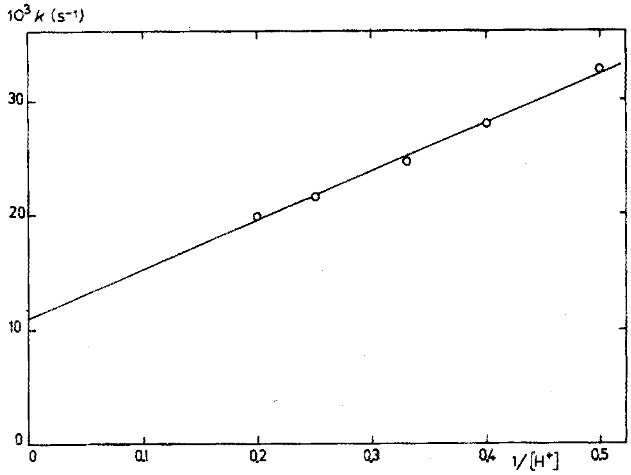


Fig. 6. The dependence of the rate of the cobalt(III)–hydroxylamine reaction on $[\mathrm{H^+}]$. $\mu = 5$, [Co(III)] $= 1\cdot10^{-3}$ *M*, [Co(II)] $= 5\cdot10^{-3}$ *M*, $[\mathrm{NH_2OH}] = 1\cdot10^{-2}$ *M*

The pseudofirst-order rate constant, *k*, was evaluated graphically from four repeated measurements at each hydroxylamine concentration; the reproducibility of measurements was 2–3 %. The constant, *k*, increased linearly with increasing hydroxylamine concentration (Fig. 5), corresponding to first order with respect to hydroxylamine.

The rate dependence on [Co(II)] was measured with initial concentrations of cobalt(III) and hydroxylamine of $1 \cdot 10^{-3}$ *M* and $1 \cdot 10^{-2}$ *M*, respectively. Within the [Co(II)] interval 0.005–0.1 *M*, the reaction rate did not depend on the cobalt(II) concentration, within experimental error.

Further, the reaction rate was inversely proportional to the hydrogen ion concentration (Fig. 6). From measurements with initial concentrations of cobalt(III) and hydroxylamine of $1 \cdot 10^{-3}$ *M* and $1 \cdot 10^{-2}$ *M*, respectively, in media 2–5 *M* in perchloric acid ($\mu = 5$), the pseudofirst-order rate constants were evaluated graphically, with a reproducibility of 3–5 % (Table VI).

TABLE VI

THE DEPENDENCE OF THE RATE OF THE COBALT(III) REACTION WITH HYDROXYLAMINE ON [H$^+$]

($\mu = 5$, [Co(III)] $= 1 \cdot 10^{-3}$ *M*, [NH_2OH] $= 1 \cdot 10^{-2}$ *M*, [Co(II)] $= 5 \cdot 10^{-3}$ *M*)

[H$^+$] (*M*)	5	4	3	2.5	2
10^3 *k* (s^{-1})	19.7	21.5	24.6	27.9	32.6
Error (s^{-1})	±0.6	±0.8	±0.9	±0.9	±1.2

DISCUSSION

The oxidation of hydroxylamine with trivalent cobalt can proceed with consumption of one to six equivalents of cobalt(III) per equivalent of hydroxylamine, depending on the ratio of the initial concentrations of the reactants. With an increasing excess of hydroxylamine, the cobalt(III) consumption decreases as far as the limiting reaction, Co(III) : $NH_2OH = 1$, expressed by the overall equation:

$$\mathrm{Co(III)} + \mathrm{NH_2OH} \rightarrow \mathrm{Co(II)} + 1/2\ \mathrm{N_2} + \mathrm{H_2O} + \mathrm{H^+}$$

In the presence of a 6-fold excess of cobalt(III), the hydroxylamine oxidation proceeds as far as nitrate, with consumption of six equivalents of cobalt(III). In the presence of a smaller excess of cobalt(III) or a small excess of hydroxylamine (1–4-fold), the oxidation of hydroxylamine proceeds with the consumption of 5–2 equivalents of cobalt(III). The reaction products are again nitrate and a colourless gas, which is apparently nitrogen and not nitrous oxide. The oxidation of the nitroxyl formed must be faster than its dimerization with formation of N_2O; for in the presence of equivalent concentrations of cobalt(III) and hydroxylamine ([Co(III)] = 6[NH_2OH]), the hydroxylamine oxidation proceeds quantitatively to nitrate.

The hydroxylamine oxidation to nitrogen was first order with respect to cobalt(III) and hydroxylamine and the rate was inversely proportional to the hydrogen ion concentration. The reaction rate did not depend on the cobalt(II) concentration. The hydroxylamine oxidation to nitrate was also first order with respect to cobalt(III), but, at certain initial concentrations of hydroxylamine, the overall reaction was first order, *i.e.* zero order with respect to hydroxylamine, although the reaction rate increased with increasing initial concentration of hydroxylamine. The reaction rate was independent of $[H^+]$ but increased linearly with increasing cobalt(II) concentration.

In agreement with the conclusions given above and by analogy with the cerium(IV)–hydroxylamine reaction[7], the following mechanism is proposed for the oxidation of hydroxylamine:

$$Co_{aq}^{3+} \overset{K_h}{\rightleftharpoons} CoOH_{aq}^{2+} + H^+ \qquad (1)$$

$$CoOH^{2+} + NH_3OH^+ \xrightarrow{k_1} Co(II) + NH_2O\cdot + H^+ + H_2O \qquad (2)$$

$$Co^{3+} + NH_3OH^+ \xrightarrow{k_2} Co(II) + NH_2O\cdot + 2\,H^+ \qquad (3)$$

$$2\,NH_2O\cdot \xrightarrow{k_3} N_2 + 2\,H_2O \qquad (4)$$

$$Co_{aq}^{2+} + Co_{aq}^{3+} \rightleftharpoons (Co^{3+}H_2O\,Co^{2+})_{aq} \qquad (5)$$

$$(Co^{3+}H_2O\,Co^{2+})_{aq} + NH_2O\cdot \xrightarrow{k_4} 2\,Co(II) + HNO + H^+ \qquad (6)$$

$$HNO + 4\,Co(III) + 2\,H_2O \rightarrow NO_3^- + 4\,Co(II) + 5\,H^+ \qquad (7)$$

For the rate constants of particular steps, in agreement with the above conclusions of the kinetic analysis, it holds that $k_3 < k_4 < k_1 + k_2$. Step (7) includes several successive fast steps.

The dependence of step (2) on $[H^+]$ is caused by the hydrolysis of trivalent cobalt (step 1), since hydroxylamine is, in the medium used (2–5 M $HClO_4$) present solely in the protonated form[7], NH_3OH^+. Step (6) is independent of $[H^+]$ because the complex $(Co^{3+}H_2O\,Co^{2+})_{aq}$ is formed by unhydrolyzed cobalt(III) ions whose concentration predominates in the solution. The catalysis by cobalt(II) is explained in the same way as that in the hydrazine oxidation[2], by the mechanism proposed earlier for hydroxylamine oxidation catalysis[1]. However, it is now assumed that step (6) and possibly even succeeding steps, are catalyzed.

The rate-determining steps of the one-electron hydroxylamine oxidation are steps (2) and (3), and the following rate equation corresponds to the reaction:

$$v = -\frac{d[Co(III)]}{dt} = k_1 K_h [Co(III)] \frac{1}{[H^+]} [NH_2OH] + k_2 [Co(III)][NH_2OH]$$

From the dependence of the constant, k, ($k = k_1 K_h([NH_2OH]/[H^+]) + k_2[NH_2OH]$) on $1/[H^+]$ (Fig. 6), the values $k_1 K_h = 4.25 \pm 0.17$ $[s^{-1}]$ and $k_2 = 1.1$ $[M^{-1}\,s^{-1}]$ were calculated ($k_1 K_h = tg\alpha/[NH_2OH]$; $k_2 = y/[NH_2OH]$ where $tg\alpha$ is the slope of the straight line in Fig. 6 and y is its intercept). If $K_h \lesssim 5 \cdot 10^{-3}\,[M]$, $k_1 \gtrsim 825\,[M^{-1}\,s^{-1}]$.

In the presence of excess of cobalt(III), hydroxylamine is further oxidized, and the radical $NH_2O\cdot$ does not dimerize but is oxidized in several steps to nitrate. Since this oxidation depended on the cobalt(II) concentration and not on $[H^+]$, steps (2) and (3) are not rate-determining, but step (6) is. Since, at a certain initial hydroxylamine concentration, the overall reaction was first order and, further, the rate dependence on initial $[NH_2OH]$ did not pass through the origin (Fig. 2), it is obvious that step (6) is preceded by a slow equilibrium when the $NH_2O\cdot$ radical forms an active transition complex ($NH_2O\cdot \rightleftharpoons X\cdot$). This then reacts in step (6) instead of the radical $NH_2O\cdot$. If the steady-state approximation is considered, the complex is present at a low constant concentration during the reaction. Then the rate does not depend on the instantaneous hydroxylamine concentration but increases with increasing initial hydroxylamine concentration.

The hydroxylamine oxidation to nitrate is, therefore, a complicated reaction and only a probable mechanism can be proposed. The catalysis by cobalt(II) ions observed earlier[1] was verified and the proposed mechanism of the catalysis applies, although a new overall mechanism of the six-electron oxidation is proposed, in agreement with the study of the hydroxylamine one-electron oxidation. This is not catalyzed by cobalt(II) since, as we suppose, hydroxylamine forms a transition complex with cobalt(III) which further undergoes an oxidation–reduction reaction. A cobalt(III) complex with hydroxylamine has also been assumed in the hydroxylamine oxidation in sulphuric acid medium[6]. In the present case, the rate-determining step would be complex formation; the subsequent redox reaction is then very fast, so that the complex could neither be detected spectrophotometrically nor be proven by kinetic analysis. In the oxidation of hydroxylamine with cerium(IV)[7], the course of which is very similar to that of the oxidation with cobalt(III), complex formation between cerium(IV) and hydroxylamine in a sulphuric acid medium was again assumed.

SUMMARY

The kinetics of hydroxylamine oxidation with cobalt(III) in a perchloric acid medium were studied by classical spectrophotometry; a special adapter was used for the Unicam SP800 spectrophotometer. By following the rate of the first step, *i.e.* the oxidation to nitrogen, the mechanism of the several-electron oxidation of hydroxylamine with variable stoichiometry, depending on the initial ratio of the reactants was also solved. In the presence of a 6-fold excess of hydroxylamine, the one-electron oxidation to nitrogen proceeded quantitatively; with a 6-fold excess of cobalt(III), hydroxylamine was oxidized to nitrate, consuming 6 Co(III). The one-electron hydroxylamine oxidation was first order with respect to both the reactants and was inversely proportional to $[H^+]$. The oxidation to nitrate was independent of $[H^+]$ but was catalyzed by cobalt(II). A probable mechanism of the oxidation was proposed and the rate constants for the one-electron hydroxylamine oxidation were calculated.

RÉSUMÉ

Une étude par spectrophotométrie classique est effectuée sur la cinétique d'oxydation de l'hydroxylamine avec cobalt(III), en milieu acide perchlorique. Un dispositif spécial est utilisé avec le spectrophotomètre Unicam SP-800. On propose un mécanisme d'oxydation.

ZUSAMMENFASSUNG

Die Kinetik der Oxidation von Hydroxylamin mit Kobalt(III) in perchlorsaurem Medium wurde durch klassische Spektrophotometrie untersucht; es wurde

das Spektrophotometer Unicam SP800 mit einem speziellen Adapter verwendet. Durch Messung der Geschwindigkeit der ersten Stufe, der Oxidation zum Stickstoff, wurde der Mechanismus der Oxidation von Hydroxylamin, die mit einer unterschiedlichen Anzahl von Elektronen bei variabler Stöchiometrie als Funktion des Anfangsverhältnisses der Reaktanten verläuft, ebenfalls geklärt. In Gegenwart eines 6-fachen Überschusses von Hydroxylamin verlief die Einelektronen-Oxidation zum Stickstoff quantitativ; bei einem 6-fachen Überschuss von Kobalt(III) wurde Hydroxylamin zum Nitrat oxidiert, wobei 6 Co(III) verbraucht wurden. Die Einelektronen-Oxidation des Hydroxylamins war in Bezug auf beide Reaktanten erster Ordnung und umgekehrt proportional $[H^+]$. Die Oxidation zum Nitrat war unabhängig von $[H^+]$, wurde aber durch Kobalt(II) katalysiert. Es wurde ein wahrscheinlicher Mechanismus der Oxidation vorgeschlagen, und die Geschwindigkeitskonstanten für die Einelektronen-Oxidation des Hydroxylamins wurden berechnet.

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EINE KINETISCH–KATALYTISCHE KONTINUIERLICHE ANALYSENMETHODE UNTER VERWENDUNG EINER DURCHFLUSSZELLE

BESTIMMUNG VON JODID, QUECKSILBER, MANGAN UND BLEI

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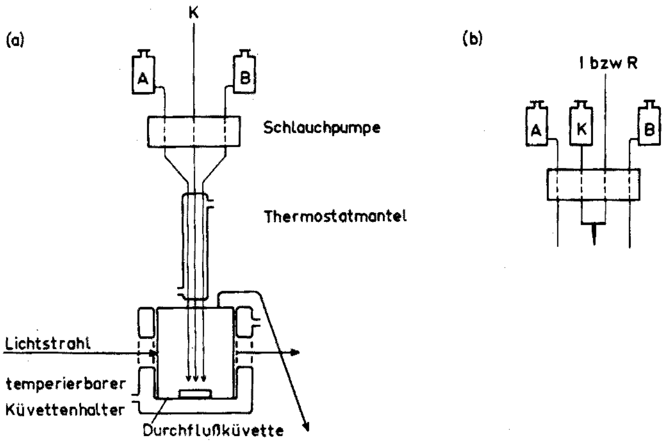
Analysenmethoden unter Verwendung katalysierter Reaktionen sind in der analytischen Chemie von Interesse, vor allem wegen ihrer hohen Empfindlichkeit. Alle kinetisch–katalytischen Methoden beruhen letztlich in irgendeiner Weise auf der Messung der Zunahme der Reaktionsgeschwindigkeit durch den Katalysator. Dazu steht eine Vielzahl der verschiedensten methodischen Möglichkeiten zur Verfügung. Dabei kann man wohl zunächst zwischen "geschlossenen" und "offenen" Systemen unterscheiden. Geschlossene Systeme sind solche, bei denen während des Ablaufs der katalysierten Reaktion selbst von aussen kein Eingriff auf die Reaktion erfolgt[1]; es werden weder Reaktionspartner zu—noch Reaktionsprodukte abgeführt, sobald die katalysierte Reaktion gestartet wurde. Bei den offenen Systemen hingegen werden Reaktionspartner während des Ablaufs der Reaktion hinzugefügt[2], oder Reaktionsprodukte abgeführt[3] oder beides. Vor allem die zuletzt erwähnten Methoden, die Strömungsmethoden, sind im Hinblick auf die steigende Tendenz zur Automatisierung in einigen Teilbereichen der analytischen Chemie von besonderem Interesse.

Die von Hartridge und Roughton[4] zu reaktionskinetischen Untersuchungen beschriebene, kontinuierliche Strömungsmethode wurde zur Bestimmung der Konzentration von Katalysatoren[5] und zur Ermittlung von Substratkonzentrationen unter Verwendung enzymkatalysierter Reaktionen weiter entwickelt[6,7]. Zu kinetischen Untersuchungen mässig schneller Reaktionen und bei kontinuierlichen Prozessen in der Industrie wird zuweilen eine andere Strömungsmethode angewendet[8]; dabei dient eine Durchflusszelle als Mischkammer, Reaktionsgefäss und in manchen Fällen auch als Messzelle ("stirred tank reactor", "capacity flow cell"). In der vorliegenden Arbeit wird nun eine kontinuierliche Analysenmethode zur Bestimmung von Katalysatoren beschrieben, die auf der Anwendung einer derartigen Durchflusszelle beruht.

Die Reaktionspartner A, B und der zu bestimmende Katalysator K einer katalysierten Reaktion strömen gesondert mit konstanter Geschwindigkeit in eine Durchflusszelle und werden dort mit einem Rührer—im Idealfall augenblicklich und vollständig—durchmischt; die resultierende Lösung verlässt hernach wieder kontinuierlich die Zelle (siehe Abb. 1). In diesem System stellt sich ein stationärer Zustand ein, d.h. die Zusammensetzung der Lösung in der Zelle ist an jeder Stelle



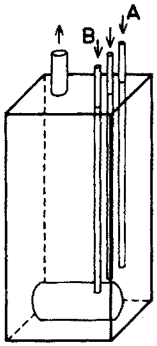


Abb. 1. Schematische Darstellung der Versuchsanordnung. (a) Bestimmung eines Katalysators K; (b) Bestimmung eines Inhibitors I beziehungsweise eines Reaktivators R.

Abb. 2. Durchflusszelle.

gleich. Wird die Konzentration eines Reaktionspartners, A, gemessen, so stellt diese im stationären Zustand unter gegebenen Bedingungen ein Mass für die Konzentration des Katalysators K dar und kann zu dessen Bestimmung herangezogen werden. Je höher die Katalysatorkonzentration ist, je schneller also die Reaktion abläuft, desto geringer ist die stationäre Konzentration von A und umgekehrt. Selbstverständlich besteht auch die Möglichkeit, aus der Messung der Konzentration eines Reaktionsproduktes die Katalysatorkonzentration zu ermitteln.

Substanzen, welche die Aktivität des Katalysators in definierter Weise verringern (Inhibitoren), können mit dieser Methode indirekt bestimmt werden. Ebenso sind Substanzen, welche einen durch Maskierung (z.B. Komplexbildung) inhibierten Katalysator in Freiheit setzen (demaskieren, reaktivieren) auf diese Weise bestimmbar.

Zur Beschreibung der Verhältnisse in der Durchflusszelle während des stationären Zustandes dient folgende Massenbilanz in Bezug auf A[9]: Die Anzahl der Mole, die im Zeitelement dt in die Zelle gelangen, ist gleich der Summe sowohl der Mole, die im selben Zeitraum die Zelle wieder verlassen, als auch der Mole, die im Volumen V durch Reaktion verbraucht werden.

$$u\cdot[\mathrm{A}]_0\cdot\mathrm{d}t = u\cdot[\mathrm{A}]_s\cdot\mathrm{d}t + r\cdot V\cdot\mathrm{d}t \qquad (1)$$

wobei
u = gesamte Strömungsgeschwindigkeit ($\mathrm{l\,s^{-1}}$)
V = Volumen der Durchflusszelle (l)
$[\mathrm{A}]_0$ = Konzentration von A an der Eintrittsstelle der drei Ströme ($\mathrm{Mol\,l^{-1}}$)
$[\mathrm{A}]_s$ = Konzentration von A im stationären Zustand ($\mathrm{Mol\,l^{-1}}$)
r = Reaktionsgeschwindigkeit im stationären Zustand ($\mathrm{Mol\,l^{-1}\,s^{-1}}$).

Zu dieser Methode kann prinzipiell jede katalysierte Reaktion unabhängig von ihrer Reaktionsordnung verwendet werden. Im folgenden soll der Fall einer katalysierten Reaktion pseudo-erster Ordnung

$$-\frac{d[A]}{dt} = k^* \cdot [K] \cdot [A] \qquad (2)$$

behandelt werden; dabei wird die Konzentration von B genügend gross gegenüber der von A gewählt. Unter den im stationären Zustand herrschenden Bedingungen nimmt Gleichung (2) folgende Form an

$$r = k^* \cdot [K] \cdot [A]_s \qquad (3)$$

Nach Einsetzen von Gleichung (3) in (1) und entsprechender Umformung ergibt sich:

$$\frac{1}{[A]_s} = \frac{1}{[A]_0} + \frac{k^* \cdot V}{[A]_0 \cdot u} \cdot [K] \qquad (4)$$

Es besteht also eine lineare Beziehung zwischen $1/[A]_s$ und der Konzentration des Katalysators K, da alle restlichen Grössen in Gleichung (4) konstant sind. Die Konzentration von A wird in der vorliegenden Arbeit photometrisch gemessen. In diesem Fall besteht ebenfalls eine lineare Beziehung zwischen dem reziproken Wert der im stationären Zustand gemessenen Extinktion E_s und der Katalysatorkonzentration, sofern das Lambert–Beer-Gesetz gültig ist.

KONTINUIERLICHE BESTIMMUNG VON JODID UND QUECKSILBER(II)

Die Bestimmung von Jodid beruht auf dessen beschleunigender Wirkung bei der Reaktion[10]

$$2\ \text{Ce(IV)} + \text{As(III)} \rightarrow 2\ \text{Ce(III)} + \text{As(V)}$$

Mit diesem System lässt sich indirekt auch Quecksilber(II) bestimmen, da es die katalytische Aktivität von Jodid hemmt[11]. Unter gegebenen Bedingungen ist die durch Jodid katalysierte Reaktion erster Ordnung in Bezug auf Cer(IV) und gehorcht der allgemeinen Geschwindigkeitsgleichung einer katalysierten Reaktion pseudoerster Ordnung[12].

Experimentelles

Cer(IV)-Lösung, Arsen(III)-Lösung und die Probelösung werden mittels einer Schlauchpumpe (Sigmamotor Inc., Middleport, Modell T8) kontinuierlich mit jeweils gleicher Strömungsgeschwindigkeit in die Durchflusszelle gepumpt und dort mit einem Magnetrührer durchmischt (hohe Tourenzahl!). Die Transmission der Cer(IV)-Lösung in der Zelle (gelb) wird photometrisch bei 420 nm (Spektralphotometer "PMQ II", Zeiss, Oberkochen) gemessen und in Abhängigkeit von der Zeit mit einem Schreiber registriert (Abb. 1).

Die Durchflusszelle wurde aus einer im Handel erhältlichen Glasküvette mit einer Schichtlänge von 20 mm (H-Küvette, Zeiss) hergestellt. Auf die Küvette wurde ein Glasdeckel mit vier Bohrungen aufgeklebt (Abb. 2). Die drei seitlich, in Reihe angeordneten Bohrungen enthalten drei Zuführungsschläuche (Polyäthylen, Innen ∅ 1 mm), die direkt über einem teflonbeschichteten Magnetrührstab (Länge 15 mm) enden; die vierte Bohrung enthält einen PVC-Schlauch (Innen ∅ 2 mm) für die ausfliessende Lösung. Das Gesamtvolumen der Durchflusszelle abzüglich des Rührstabes und der eintauchenden Schläuche beträgt 13.4 ml.

Die Zuführungsschläuche enthalten jeweils ein dazwischengeschaltetes Stück Tygonschlauch (Innen ∅ 1.59 mm, Wandstärke 1.59 mm), das in die Schlauchpumpe eingelegt wird. Kurz vor Eintritt in die Zelle durchlaufen die drei Zuführungsschläuche einen Thermostatmantel (Länge 210 mm, Innen ∅ 15 mm). Die Durchflusszelle selbst befindet sich in einem temperierbaren Küvettenhalter (passend zum Spektralphotometer "PMQ II", Zeiss), der zugleich mit einem Motor für einen Magnetrührer ausgestattet war (Abb. 1).

Um über einen längeren Zeitraum eine konstante und reproduzierbare Anzeige des Messwertes zu erzielen, soll das Spektralphotometer ständig betriebsbereit gehalten und zwischen den Messungen nicht ausgeschaltet werden; ferner soll die Schwankung der Raumtemperatur möglichst gering gehalten werden, da sonst das thermische Gleichgewicht des Messgerätes gestört wird, was zu Fehlern in der Anzeige führen kann.

Lösungen. Cer(IV)-sulfatlösung, $3.75 \cdot 10^{-3}$ *M* in 1 *M* Schwefelsäure.

Arsen(III)-Lösung, $2.5 \cdot 10^{-2}$ M (4.946 g $As_2O_3 + 50$ ml 1 *M* NaOH + 250 ml 4 *M* H_2SO_4 ad 2000 ml).

Die hochverdünnten Jodid- und Quecksilber(II)-Lösungen wurden aus entsprechenden Stammlösungen durch Verdünnung mit bidestilliertem Wasser täglich frisch hergestellt und in Polyäthylenflaschen aufbewahrt. Die zur Verdünnung der Stammlösungen verwendeten Glasgefässe waren zuvor zwecks Vermeidung von Adsorptionsverlusten zwei Tage mit den entsprechenden Lösungen in Berührung.

Bestimmung von Jodid. Vor Beginn einer Bestimmungsserie wird reines Wasser durch die Zelle gepumpt und die Grundlinie, entsprechend 100% Transmission, bei 420 nm aufgenommen. Dies wird jeweils nach 1 bis 1.5 Stunden wiederholt, wobei die Geräteinstellung bei Bedarf nachgeregelt wird. Innerhalb dieses Zeitraumes soll die Abweichung nicht mehr als 1% Transmission betragen. Die Strömungsgeschwindigkeit in der Durchflusszelle, welche der Summe der in jedem Zuführungsschlauch herrschenden, gleichen Strömungsgeschwindigkeit entspricht, beträgt bei der Bestimmung von Jodid 13.2 ml min^{-1} (1 Schlauch = 4.4 ml min^{-1}). Cer(IV)-Lösung und Arsen(III)-Lösung befinden sich im Bad des Thermostaten (Temperatur 30.0°).

Während einer Serie von Bestimmungen wird der Schlauch für die Probe von Hand in das jeweilige Gefäss eingeführt, jedoch könnte hierzu selbstverständlich auch ein geeigneter mechanischer Probenwechsler verwendet werden. Nach Erreichen des stationären Zustandes im System wird die gemessene Transmission aus der registrierten Kurve graphisch extrapoliert, anhand einer Tabelle in die reziproke Extinktion umgewandelt und die unbekannte Probemenge unter Verwendung einer Eichkurve ermittelt. Zur Erstellung der Eichkurve für die Bestimmung von Jodid werden 10 Messungen im Bereich von 50 ng J^- ml^{-1} bis 5 μg J^- ml^{-1} durchgeführt und jeweils die reziproke Extinktion gegen die entsprechende Jodidmenge graphisch aufgetragen.

Bestimmung von Quecksilber. Zur Bestimmung von Quecksilber wird eine jeweils gleiche Standard-Kaliumjodidlösung ($1.5 \cdot 10^{-5}$ *M*) verwendet. Die Schläuche für die Standard-Kaliumjodidlösung und die Quecksilberlösung sind an ein T-Stück aus kapillarem Glasrohr (Innen ∅ 1 mm, Schenkellänge 20 mm) angeschlossen. Die Lösungen werden dort durchmischt und die resultierende Lösung durchströmt hernach vor Eintritt in die Durchflusszelle eine Verzögerungsstrecke, um eine vollständige Reaktion von Jodid mit Quecksilber zu gewährleisten (Polyäthylen, Länge 400 mm, Innen ∅ 1 mm, davon 210 mm thermostatiert, Abb. 1). Die Strömungsgeschwindigkeit in der Durchflusszelle beträgt 17.2 ml min^{-1} (1 Schlauch $=4.4$ ml min^{-1}). Ansonsten erfolgt die Bestimmung von Quecksilber in der gleichen Weise wie die für Jodid. Zur Aufnahme der Eichkurve für Quecksilber werden 10 Messungen im Bereich von 0.2 μg Hg(II) ml^{-1} bis 1.4 μg Hg(II) ml^{-1} durchgeführt.

Ergebnisse und Diskussion

Auf diese Weise wurden zahlreiche Bestimmungen durchgeführt, wobei kontinuierlich bis zu acht Stunden gemessen wurde. Ein Ausschnitt aus einer Kurve, welche die Abhängigkeit der Transmission von der Zeit für unterschiedliche Katalysatorkonzentrationen (Jodid) zeigt, ist in Abb. 3 wiedergegeben. Je höher die Katalysatorkonzentrationen und je kleiner die Differenz der Konzentrationen zweier aufeinanderfolgender Proben ist, desto schneller ist der neue stationäre Zustand jeweils erreicht.

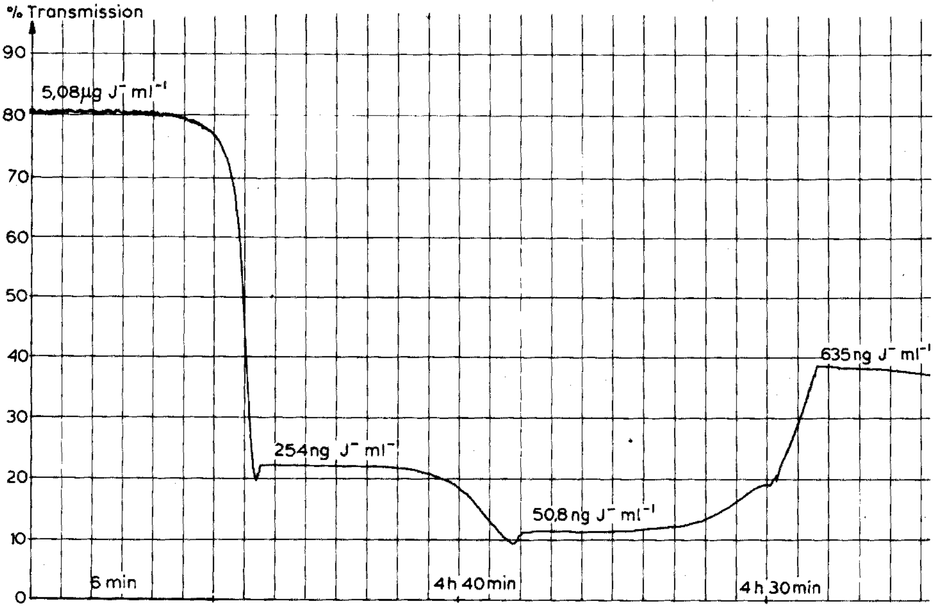


Abb. 3. Ausschnitt aus einer vom Schreiber registrierten Kurve (Bestimmung von Jodid).

Die Abhängigkeit der reziproken Extinktion ($1/E_s$) von der Katalysatorkonzentration zeigt Abb. 4. Da im vorliegenden Fall das Lambert–Beer-Gesetz für Cer(IV) erfüllt ist, war eine lineare Abhängigkeit zu erwarten (vgl. Gleichung 4). Dies wurde für den Bereich von 0.1 μg J$^-$ ml^{-1} bis 2.5 μg J$^-$ ml^{-1} experimentell bestätigt. Für höhere ebenso wie für niedrigere Jodidkonzentrationen trat nur eine geringfügige Abweichung von der geforderten Geraden auf. Bei der Bestimmung von Quecksilber(II) liegt die Konzentration des restlichen, noch katalytisch aktiven Jodids unter den genannten Bedingungen immer innerhalb des linearen Teils der in Abb. 4 wiedergegebenen Kurve, sodass die Eichkurve für Quecksilber eine Gerade darstellt.

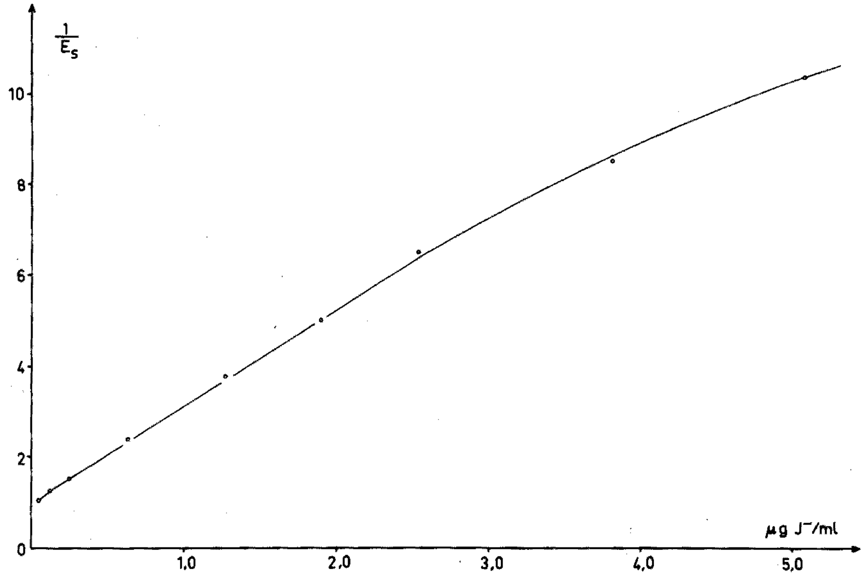


Abb. 4. Abhängigkeit des $1/E_s$-Wertes von der Jodidkonzentration. Reaktionsbedingungen s. Text.

TABELLE 1

BESTIMMUNG VON JODID UND QUECKSILBER

J^- (µg ml^{-1}) gegeben	*J^- (µg ml^{-1}) gefunden*	*Relativer Fehler (%)*	*Hg(II) (µg ml^{-1}) gegeben*	*Hg(II) (µg ml^{-1}) gefunden*	*Relativer Fehler (%)*
0.051	0.046	− 9.8	0.160	0.185	+15.6
0.127	0.142	+11.8	0.201	0.204	+ 1.5
0.254	0.250	− 1.6	0.201	0.188	−6.5
0.635	0.646	+ 1.7	0.401	0.382	−4.7
1.02	1.05	+ 2.9	0.602	0.625	+3.8
1.27	1.27	± 0	0.802	0.779	−2.9
1.90	1.95	+ 2.6	0.802	0.813	+1.4
2.54	2.46	− 3.1	1.20	1.20	± 0
3.81	3.95	+ 3.7	1.40	1.41	+ 0.7
5.08	4.84	− 4.7	1.40	1.40	± 0

Bei den Messungen im Bereich von 50 ng J^- ml^{-1} bis 5 µg J^{-1} ml^{-1} stellt sich der stationäre Zustand entsprechend der Katalysatorkonzentration nach etwa zwei bis sieben Minuten ein, sodass sechs bis acht Bestimmungen pro Stunde durchgeführt werden konnten. Einige wenige Ergebnisse aus einer grossen Zahl von Einzelbestimmungen sind in Tabelle I wiedergegeben. Die Standardabweichung für den Bereich von 0.25 µg J^- ml^{-1} bis 2.5 µg J^- ml^{-1}, berechnet aus 25 Messungen nach einer für Eichmessungen beschriebenen Methode[13], beträgt ± 0.043 µg J^- ml^{-1}.

Einige Ergebnisse für Quecksilberbestimmungen sind ebenfalls in Tabelle I aufgeführt. Aus 25 Messungen im Bereich von 0.2 µg Hg ml^{-1} bis 1.4 µg Hg ml^{-1} wurde die Standardabweichung zu ±0.022 µg Hg ml^{-1} berechnet. Bei der Bestimmung von Quecksilber(II) ist es ratsam, die Eichkurve vor jeder längeren Bestimmungsserie mit wenigen Messungen zu überprüfen, da durch geringfügige Änderungen in der Steilheit der Eichgeraden vor allem bei geringen Quecksilberkonzentrationen grössere Fehler auftreten können.

KONTINUIERLICHE BESTIMMUNG VON MANGAN

Die Oxidation von Alizarin S durch Wasserstoffperoxid wird durch Mangan stark beschleunigt[14]. Die Transmission der Alizarin S-Lösung in der Durchflusszelle wird während des stationären Zustandes bei 335 nm gemessen und dient zur Ermittlung der zu bestimmenden Mangankonzentration.

Die im vorigen Teil der Arbeit beschriebene Versuchsanordnung wurde geringfügig abgeändert. Um den Bedarf an Probemenge pro Bestimmung zu verringern, wurde das Volumen der Durchflusszelle verkleinert und auch die Strömungsgeschwindigkeit vermindert. Die Durchflusszelle (Schichtlänge 10 mm, Volumen 1.7 ml, Abb. 2) befand sich in einem passenden, temperierten Aluminumblock. Als Schlauchpumpe wurde eine Buchler-Pumpe (Buchler Instruments, Fort Lee, Modell 2-6200) verwendet. Die drei Zuführungsschläuche bestanden aus Tygon (Innen ∅ 0.79 mm, Wandstärke 0.79 mm) und aus einem anschliessenden, in einem Thermostatmantel befindlichen Stück Polyäthylenschlauch (Länge 210 mm, Innen ∅ 1 mm).

Lösungen

Alizarin S-Stammlösung, 10^{-2} *M*.

Ammoniumcarbaminatlösung, 1.02 *M* (Merck p.a.).

Wasserstoffperoxidlösung, $7.5 \cdot 10^{-2}$ *M*. Die in einer Polyäthylenflasche aufbewahrte Lösung blieb einige Tage stabil.

Die zur Verdünnung und Aufbewahrung von Manganlösung verwendeten Glasgefässe wurden zuvor mit konz. Salzsäure gereinigt. Zur Vermeidung von Adsorptionsverlusten waren alle Glassgefässe zur Herstellung und Aufbewahrung hochverdünnter Lösungen zwei Tage mit den entsprechenden Lösungen in Berührung.

Durchführung und Ergebnisse

Die Grundlinie (= 100% Transmission) wird mit reinem Wasser bei einer Wellenlänge von 335 nm aufgenommen. Dies wird während einer Serie von Bestimmungen jeweils nach 1 bis 1.5 Stunden wiederholt (vgl. Bestimmung von Jodid). Die verwendete Alizarin S-Lösung (3 ml Alizarin S-Stammlösung + 18 ml Ammoniumcarbaminatlösung ad 100 ml) wird vor jeder Bestimmungsserie frisch hergestellt. Die Strömungsgeschwindigkeit in der Durchflusszelle beträgt bei der Bestimmung von Mangan 1.83 ml min^{-1} (1 Schlauch = 0.61 ml min^{-1}). Alle Reagenzlösungen befinden sich im Bad des Thermostaten (30.0°). Die Auswertung der Messergebnisse geschieht in der bereits für Jodid beschriebenen Weise. Die Eichkurve für Mangan wird aus 10 Messungen im Bereich von 10 ng Mn ml^{-1} bis 600 ng Mn ml^{-1} erstellt.

Einige Ergebnisse aus einer Serie von Manganbestimmungen, die sich insgesamt über 10 Stunden erstreckte, sind in Tabelle II aufgeführt.

TABELLE II

BESTIMMUNG VON MANGAN

Mn (ng ml^{-1}) gegeben	*Mn (ng ml^{-1}) gefunden*	*Relativer Fehler (%)*
10	12	+20.0
25	27	+ 8.0
50	53	+ 6.0
75	72	− 4.0
100	95	− 5.0
200	203	+ 1.5
300	308	+ 2.7
400	407	+ 1.8
500	521	+ 4.2
600	593	− 1.2

KONTINUIERLICHE BESTIMMUNG VON BLEI

Neben der Bestimmung von Katalysatoren und Inhibitoren eröffnet sich eine weitere interessante Möglichkeit der Anwendung katalysierter Reaktionen: Liegt der Katalysator in inaktiver Form, z.B. komplex gebunden, in der Reaktionslösung vor, so können Substanzen bestimmt werden, welche den Katalysator durch Demaskierung in Freiheit setzen, ihn also reaktivieren. Hierauf beruht die im folgenden beschriebene Bestimmung von Blei. Die katalytische Aktivität von Mangan, das die Oxidation von Alizarin S durch Wasserstoffperoxid stark beschleunigt[14], wird durch DCyTE (*trans*-1,2-Diamino-cyclohexan-N,N,N',N'-tetraessigsäure) stark herabgesetzt. Blei vermag nun Mangan aus dem Komplex mit DCyTE zu verdrängen und lässt sich auf diese Weise in direkt bestimmen.

Lösungen

Zusätzlich zu den bei der Bestimmung von Mangan beschriebenen Lösungen werden noch folgende Lösungen verwendet:

Mangan–DCyTE-Stammlösung, 10^{-2} *M*. Diese Lösung wird aus einer 0.1 *M* Manganlösung und einer 0.1 *M* DCyTE-Lösung (Dinatrium-salz der *trans*-1,2-Diamino-cyclohexan-N,N,N',N'-tetraessigsäure) durch entsprechende Verdünnung wöchentlich frisch hergestellt.

Natriumcitrat–Salzsäure-Puffer, *pH* 4.0. 44 ml 0.1 *N* Chlorwasserstoffsäure +56 ml 0.1 *M* Natriumcitrat (21.008 g Citronensäure-Monohydrat +200 ml 1 *N* Natronlauge ad 1000 ml).

Mangan–DCyTE-Lösung, $2 \cdot 10^{-5}$ *M* (*pH* 4.2). Enthält 10 ml Natriumcitrat–Salzsäure-Puffer pro 100 ml.

Die zur Verdünnung und Aufbewahrung der Mangan–DCyTE-Lösung verwendeten Glassgefässe werden zuvor mit konz. Salzsäure gereinigt.

Durchführung

Die zur Bestimmung von Blei verwendete Alizarin S-Lösung (4 ml Alizarin S-Stammlösung +45 ml Ammoniumcarbaminatlösung ad 100 ml) wird alle drei

Stunden frisch bereitet, da die Stabilität der Alizarin S-Lösung mit zunehmender Ammoniumcarbaminatkonzentration abnimmt. Die Bleilösung und die Lösung des Mangan–DCyTE-Komplexes (2.10^{-5} M) werden in einem T-Stück vereinigt und mittels eines Polyäthylenschlauchs als Verzögerungsstrecke in die Durchflusszelle eingeführt (Länge 3340 mm, Innen ∅ 1 mm, "Verzögerungszeit" ≈ 2 min). Die Strömungsgeschwindigkeit in der Durchflusszelle beträgt 2.48 ml min^{-1} (1 Schlauch =0.62 ml min^{-1}). Ansonsten erfolgt die Bestimmung von Blei in der für Mangan beschriebenen Weise. Die Eichkurve für Blei wird mit 7 Messungen im Bereiche von 0.1 µg Pb ml^{-1} bis 2.0 µg Pb ml^{-1} aufgenommen.

Ergebnisse und Diskussion

Da die Geschwindigkeit der Reaktion von Blei mit dem Mangan–DCyTE-Komplex in verdünnter Lösung stark pH abhängig ist, wurde die Mangan–DCyTE-Lösung in geeigneter Weise gepuffert. Durch eine genügend hohe Ammoniumcarbaminatkonzentration in der Reaktionslösung wurde die Pufferkapazität des gesamten Systems soweit vergrössert, dass sich der Puffer der zufliessenden Mangan–DCyTE-Lösung insgesamt nicht störend bemerkbar machte.

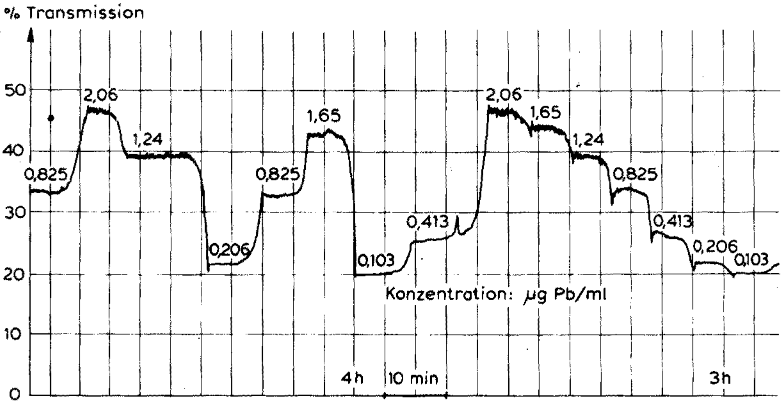


Abb. 5. Ausschnitt aus einer vom Schreiber registrierten Kurve (Bestimmung von Blei). $2 \cdot 10^{-5}$ M Mn–DCyTE.

Abb. 5 zeigt einen Ausschnitt aus einer Kurve, welche die Abhängigkeit der Transmission von der Zeit für unterschiedliche Bleikonzentrationen wiedergibt.

Für den unteren Konzentrationsbereich ergab sich eine lineare Abhängigkeit des $1/E_s$-Wertes von der Bleikonzentration. Bei hohen Bleikonzentrationen, die einer hohen Konzentration an katalytisch aktivem Mangan entsprechen, lag der gemessene $1/E_s$-Wert zu tief (vgl. Bestimmung von Jodid). In Tabelle III sind einige wenige Ergebnisse aus einer Serie von Bleibestimmungen wiedergegeben, die sich über 7 Stunden erstreckte. Die Standardabweichung für den Bereich von 0.1 µg Pb ml^{-1} bis 0.8 µg Pb ml^{-1} wurde aus 24 Messungen zu ±0.019 µg Pb ml^{-1} berechnet.

Diese Methode bietet eine gute Möglichkeit zur Automatisierung von Analysenverfahren. Vielleicht ist eine solche automatisierbare Methode für die heute so vieldiskutierte Problematik des Umweltschutzes von Interesse.

TABELLE III

BESTIMMUNG VON BLEI

Pb (μg ml⁻¹) gegeben	*Pb (μg ml⁻¹) gefunden*	*Relativer Fehler (%)*
0.103	0.114	+10.7
0.103	0.094	− 8.7
0.206	0.199	− 3.4
0.413	0.433	+ 4.8
0.825	0.800	− 3.0
0.825	0.822	− 0.4
1.24	1.19	− 4.0
1.65	1.62	− 1.8
1.65	1.73	+ 4.8
2.06	2.08	+ 1.0

ZUSAMMENFASSUNG

Es wird eine kontinuierliche, kinetisch–katalytische Analysenmethode beschrieben. Die Reaktionspartner einer katalysierten Reaktion und der zu bestimmende Katalysator fliessen kontinuierlich in drei gesonderten Strömen in eine Durchflusszelle und werden dort durchmischt. In diesem System stellt sich ein stationärer Zustand ein. Die jeweils stationäre Konzentration eines geeigneten Reaktionspartners wird photometrisch gemessen und stellt ein Mass für die Konzentration der katalytisch aktiven Substanz dar. So wird Jodid aufgrund seiner beschleunigenden Wirkung auf die Reaktion von Cer(IV) mit Arsen(III) kontinuierlich im p.p.b.-bis p.p.m.-Bereich bestimmt. Quecksilber(II) hemmt die katalytische Wirkung von Jodid und kann dadurch indirekt bestimmt werden. Mangan wird im p.p.b.-Bereich aufgrund seiner katalytischen Wirkung auf die Oxidation von Alizarin S durch Wasserstoffperoxid bestimmt. Blei vermag Mangan aus einem katalytisch inaktiven Komplex mit DCyTE zu verdrängen und kann dabei ebenfalls kontinuierlich im p.p.b.-bis p.p.m.-Bereich bestimmt werden.

SUMMARY

A continuous kinetic–catalytic method of analysis is described. The reactants involved in a catalytic reaction and the catalyst to be determined flow continuously in three separate streams to a flow-through cell and are mixed there. In this system, a "stationary" condition is produced. In each case the "stationary" concentration of a suitable reactant is measured spectrophotometrically, which yields a measure of the catalytically active substance. Iodide can be determined continuously in the p.p.b. to p.p.m. range by means of its catalytic action on the cerium(IV)–arsenic(III) reaction. Mercury(II) prevents this catalytic action and so can be determined indirectly. Manganese can be determined in the p.p.b. range by means of its catalytic action on the oxidation of alizarin S by hydrogen peroxide. Lead displaces manganese from its catalytically inactive complex with DCyTA and so can be determined continuously in the p.p.b. to p.p.m. range.

RÉSUMÉ

On décrit une méthode d'analyse catalytique–cinétique continue. Les réactants d'une réaction catalytique et le catalyseur à doser s'écoulent en continu, en trois courants séparés, dans une cellule où se fait leur mélange. La concentration "stationnaire" d'un réactant est mesurée spectrophotométriquement, ce qui permet le dosage de la substance catalytiquement active. Les iodures peuvent être ainsi déterminés en continu (en quantités de l'ordre du p.p.b. au p.p.m.), grâce à leur réaction catalytique sur cérium(IV)–arsenic(III). Le mercure(II) empêche cette réaction de catalyse et peut ainsi être dosé indirectement. Le manganèse peut être déterminé grâce à son action catalytique sur l'oxydation de l'alizarine S par le peroxyde d'hydrogène. Le plomb déplace le manganèse de son complexe de DCyTA, catalytiquement inactif, et peut alors être dosé indirectement de cette manière.

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EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF MICRO AMOUNTS OF BISMUTH WITH ZINC DIBENZYLDITHIOCARBAMATE

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Diethyldithiocarbamate reacts with many metal ions to give colored chelate compounds, and has been widely used for the extraction and spectrophotometric determination of such ions as copper, bismuth, nickel, etc.[1–4]. In acidic solution this reagent is very unstable and so has been used mainly in alkaline, neutral or weakly acidic media.

Several other derivatives of dithiocarbamate have also been studied analytically[3,5–7]. The authors have described previously the use of zinc dibenzyldithiocarbamate (Zn–DBDTC) for the determination of micro amounts of copper in high-purity thorium compounds[8]. It has been found that bismuth(III) also forms colored chelate compound with DBDTC by a displacement reaction with the zinc salt, which is soluble in organic solvents such as carbon tetrachloride and chloroform.

This provides the basis of a new method for the rapid extraction and spectrophotometric determination of bismuth. The present paper describes an investigation of the optimal conditions for the extraction and determination of micro amounts of bismuth with zinc–DBDTC. In the method developed, bismuth can be determined in relatively strong acid solutions, and the bismuth(III)–DBDTC chelate formed is very stable. None of the experimental conditions is highly critical.

EXPERIMENTAL

Reagents and apparatus

Standard bismuth solution (500 $\mu g\ ml^{-1}$). Dissolve 0.500 g of bismuth metal (99.999%) in small amounts of 6 *M* nitric acid and then dilute to 1 l with 1 *M* nitric acid. Prepare more dilute solutions from this stock solution by dilution.

When bismuth solution in sulfuric acid media was needed, bismuth was dissolved in 6 *M* nitric acid, and sulfuric acid was added, followed by heating to slightly white fuming, and dilution with 1 *M* sulfuric acid.

Zinc–DBDTC solution. Dissolve 0.30 g of Zn–DBDTC (B.D.H. Laboratory Chemicals) in 1 l of reagent-grade carbon tetrachloride.

All other chemicals were of reagent grade and were used without further purification.

Analytical measurements were made with a Hitachi Model EPU-2A spectrophotometer in 1-cm cells. An Iwaki KM-shaker was used.

Procedure

Transfer an aliquot of solution, containing up to 80 μg of bismuth to a 100-ml separating funnel, and add enough nitric acid and water to give a 0.3–2.5 *M* acid concentration (in the case of hydrochloric acid 0.3–4 *M* or sulfuric acid 0.3–3 *M*), in which the final total volume of aqueous phase is about 25 ml.

Add 10.0 ml of Zn–DBDTC solution and shake for 90 s. After phase separation, drain the organic solution through a filter paper (No. 5B) into the optical cell. Measure the absorbance at 370 nm against a reagent blank.

RESULTS AND DISCUSSION

Absorption spectra

The light yellowish bismuth(III)–DBDTC chelate in carbon tetrachloride exhibits absorption maxima at *ca.* 330 nm and 370 nm (Fig. 1, curve 1). Similar absorption spectra were observed in 1 *M* hydrochloric acid solution and in 1.5 *M* sulfuric acid solution. The same chelate compound is probably formed from these acid solutions.

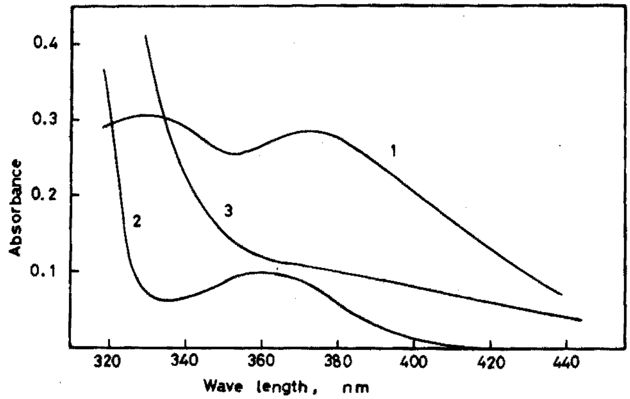

Fig. 1. Absorption spectra. (1) Spectrum of bismuth–DBDTC in carbon tetrachloride extracted from 1 *M* nitric acid solution containing 50 μg of bismuth; reference: reagent blank. (2) 0.03% Zn–DBDTC solution after shaking with 1 *M* nitric acid solution without bismuth; reference: carbon tetrachloride. (3) 0.03% Zn–DBDTC solution after shaking with 4 *M* nitric acid solution without bismuth; reference: carbon tetrachloride.

On extraction from 4 *M* nitric acid solution, the absorption spectrum of the reagent was completely changed (Fig. 1, curve 3) and the spectrum of bismuth–DBDTC chelate was not observed. These results show that in very strongly acidic solutions, the reagent is less stable and decomposition occurs.

Analytical measurements were made at 370 nm, because several other metal ions such as lead, antimony, mercury and silver could also be extracted and caused serious interference at 330 nm.

Extraction solvent

Bismuth–DBDTC chelate in chloroform showed similar absorption spectrum as in carbon tetrachloride, but each maximum was shifted about 5 nm towards a shorter wavelength. Carbon tetrachloride was preferred to chloroform because it is less soluble in water, separates well from water and gives a clear phase.

Ethyl acetate was unsuitable because the absorbance of the extract quickly decreased with time.

Reagent concentration

The extraction and spectrophotometric measurements were made with various concentrations of zinc–DBDTC for a shaking time of 90 s and a 1.5 *M* sulfuric acid solution. A 0.03% solution of zinc–DBDTC was found to be sufficient for the quantitative extraction of up to 80 μg of bismuth and for all the situations encountered in the course of this study.

Extraction time

The extraction of bismuth from aqueous solution includes the displacement reaction in the heterogeneous system, so that the extraction time is an important factor.

The absorbance of the extract from solutions containing 40 μg of bismuth was measured as a function of shaking time; 1 *M* and 3 *M* hydrochloric acid or nitric acid solutions, and 0.5 *M* and 1.5 *M* sulfuric acid solutions were tested.

With all the acids examined, constant absorbance values were obtained from 60 to 180 s, and a shaking time of 90 s was chosen for the recommended procedure. Moreover, it was shown that excessive shaking was unfavorable in the strongly acidic solutions, especially for nitric acid, because of decomposition of the reagent.

Acid concentration

The effect of different acids and their concentrations in the aqueous phase on the extraction of 40 μg of bismuth was studied. A constant absorbance value was obtained over a wide range of acidity: for hydrochloric acid in 0.3–4 *M* solutions, for nitric acid in 0.3–2.5 *M* solutions, and for sulfuric acid in 0.3–3 *M* solutions. As the acidity increased further, the absorbance decreased and finally a yellowish turbidity was observed in the organic phase, because of decomposition of the reagent.

Calibration curve

The absorbance of the extract as a function of the amount of bismuth taken followed a linear relationship obeying Beer's law for bismuth up to 80 μg.

The molar absorptivity was calculated to be 12000 at 370 nm. The same results were obtained for extraction from all the acid solutions examined, *e.g.* from 1 *M* hydrochloric acid, from 1 *M* nitric acid and from 1.5 *M* sulfuric acid.

The reproducibility was examined for 10 solutions, each containing 30 μg of bismuth. The relative standard deviation was ±1.0%.

Complex formation

The continuous variations method and mole-ratio method were applied. The composition of the reagent used was 1:2 for the molar ratio of zinc to DBDTC.

The results of the continuous variations method are shown in Fig. 2. It was found that the estimated molar ratio of bismuth to the reagent, zinc–DBDTC, was

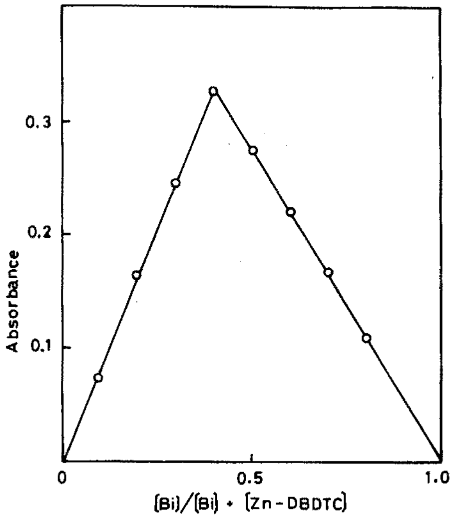

Fig. 2. Continuous variations method. (Bi)+(Zn–DBDTC)=$7.1 \cdot 10^{-7}$ *M*. Acid concentration, 1.5 *M* sulfuric acid; measurements were made at 370 nm.

2:3, so that the molar ratio of bismuth to DBDTC is 1:3. The mole-ratio method gave the same result.

Interferences

Interferences caused by foreign ions were studied by taking 30 μg of bismuth and various amounts of foreign ion. The results are summarized in Table I. Similar results were obtained in 1 *M* hydrochloric acid solution or in 1 *M* nitric acid solution.

Copper and antimony interfered seriously even at the 10 μg level. Some interference caused by lead, silver and mercury was still found for amounts at the same level as bismuth. The interference from lead and silver, however, could be removed by extraction from stronger hydrochloric acid solutions, *e.g.* 3.5 *M*, as shown in Table I, lead and silver remaining in the aqueous phase.

This suggests the possibility of a separation of bismuth from lead and silver by solvent extraction. The use of zinc–DBDTC for the extraction separation of some metal ions will be described elsewhere.

At the stated levels, no interferences were observed from the other cations. None of the anions and organic acids examined interfered even when present in quite large amounts.

Stability

The color of the bismuth diethyldithiocarbamate is unstable to light in chloroform, carbon tetrachloride and ethyl acetate, so that immediate measurement is required[4,9,10]. Bismuth–DBDTC in carbon tetrachloride, however, was found to be stable; for there was no change in absorbance for at least 5 h after extraction with no special precautions. Moreover, it was found that the reagent used was very stable and its solution in carbon tetrachloride could be used for at least two weeks after preparation.

TABLE I

EFFECT OF FOREIGN IONS

(Bismuth taken: 30 μg, extraction from 1.5 *M* sulfuric acid solution)

Foreign ion	*Added* (*μg*)	*Bi found* (*μg*)	*Relative error* (%)
Fe(III)	400	30.0	0
Cr(III)	400	30.4	1.3
Al(III)	400	30.0	0
Ni(II)	200	30.1	0.3
Ti(IV)	300	29.6	1.3
Hg(II)	50	31.5	5.0
	25	30.6	2.0
Zn(II)	400	30.0	0
Mn(II)	400	30.0	0
Ag(I)	50	33.0	10.0
	20	30.7	2.3
Ag(I)[a]	250	30.3	1.0
V(V)	400	30.0	0
Sb(III)	10	34.0	13.3
Co(II)	100	30.9	3.0
	50	30.2	0.7
Ce(IV)	400	30.2	0.7
Ca(II)	400	30.0	0
Mg(II)	400	30.0	0
Mo(VI)	100	30.9	3.0
W(VI)	300	30.2	0.7
Pb(II)	10	30.9	3.0
Pb(II)[a]	500	30.1	0.3
Cd(II)	400	30.1	0.3
Cu(II)	10	31.8	6.0
Bromide	$3 \cdot 10^3$	30.0	0
Fluoride	$3 \cdot 10^3$	30.2	0.7
Iodide	$3 \cdot 10^3$	29.9	0.3
Phosphate	$3 \cdot 10^3$	29.9	0.3
Citric acid	$3 \cdot 10^3$	30.0	0
Oxalic acid	$3 \cdot 10^3$	30.0	0
Tartaric acid	$3 \cdot 10^3$	30.1	0.3

[a] Extraction from 3.5 *M* hydrochloric acid solution.

CONCLUSIONS

Dithizone, diethyldithiocarbamate and iodide have often been used for the colorimetric determination of bismuth as colorimetric reagent[2]. The sensitivity of the method developed is less than that of the dithizone method, but is similar to that of the diethyldithiocarbamate or iodide method.

The advantages of the zinc–DBDTC method lie in the facts that bismuth can be extracted from more strongly acidic solutions over a wide range of acidity, that bismuth can be determined spectrophotometrically, and that various acids such as hydrochloric acid, nitric acid and sulfuric acid can be used for acidification.

No complicated procedure involving pH adjustment or addition of masking agents is needed, as is required in the dithizone and diethyldithiocarbamate method.

In the iodide method bismuth can also be determined in strongly acidic media. However, sulfuric acid is ordinarily used for acidification because of the effect of chloride ions[2]; moreover, a long time is required for stable color development[11,12].

On the basis of simplicity, sensitivity and stability, zinc–DBDTC proves to be a useful reagent for the rapid extraction and spectrophotometric determination of micro amounts of bismuth.

SUMMARY

A simple rapid method has been developed for the determination of micro amounts of bismuth with zinc dibenzyldithiocarbamate (DBDTC). By using 0.03% zinc–DBDTC solution in carbon tetrachloride, bismuth(III) can be extracted quantitatively over a wide range of acidity (0.3–4 *M* hydrochloric acid, 0.3–2.5 *M* nitric acid and 0.3–3 *M* sulfuric acid). The extract shows absorption maxima at *ca.* 330 nm and 370 nm, and analytical measurements are made at 370 nm. The system is stable and conforms to Beer's law up to 80 μg of bismuth; the molar absorptivity is 12000. Of the many ions tested, antimony, copper, lead, mercury and silver are also extracted and interfere.

RÉSUMÉ

On décrit une méthode spectrophotométrique simple et rapide pour le microdosage du bismuth au moyen de dibenzyldithiocarbamate (DBDTC) de zinc, en milieu tétrachlorure de carbone. Les mesures sont effectuées à 370 nm. Le système est stable et suit la loi de Beer jusqu'à 80 μg de bismuth. Le coefficient d'extinction molaire est de 12000. Parmi les ions examinés: antimoine, cuivre, plomb, mercure et argent gênent.

ZUSAMMENFASSUNG

Eine einfache und schnelle Methode für die Bestimmung von Mikromengen Wismut mit Zinkdibenzyldithiocarbamat (DBDTC) wurde entwickelt. Durch Verwendung von 0.03% Zink–DBDTC-Lösung in Tetrachlorkohlenstoff kann Wismut in einem weiten Aciditätsbereich (0.3–4 *M* Salzsäure, 0.3–2.5 *M* Salpetersäure und 0.3–3 *M* Schwefelsäure) quantitativ extrahiert werden. Der Extrakt hat Absorptionsmaxima bei *ca.* 330 nm und 370 nm; die analytischen Messungen werden bei 370 nm ausgeführt. Das System ist beständig und gehorcht dem Beerschen Gesetz bis zu 80 μg Wismut, der molare dekadische Extinktionskoeffizient ist 12000. Von den vielen untersuchten Ionen werden Antimon, Kupfer, Blei, Quecksilber und Silber ebenfalls extrahiert und stören.

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THE APPLICATION OF SALICYLALDOXIME IN SOLVENT EXTRACTION

PART II. SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH 2-(5-NITRO-2-PYRIDYLAZO)-1-NAPHTHOL AFTER SEPARATION WITH SALICYLALDOXIME

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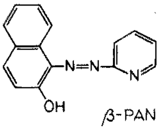
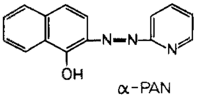
It has previously been demonstrated that copper(II) may be separated from a number of metal ions by employing solvent extraction with salicylaldoxime[1]. The extracted species is well suited for the spectrophotometric determination of copper[1-3]. The sensitivity with salicylaldoxime is fair, although less than that of some of the well established copper reagents[4].

Heterocyclic azo dyestuffs are frequently used in analytical chemistry[5]. Thus the compound 1-(2-pyridylazo)-2-naphthol (PAN, β-PAN) is recognized as a highly sensitive spectrophotometric reagent for numerous elements[5,6]. It is usually applied in connection with solvent extraction procedures. 2-(2-Pyridylazo)-1-naphthol (α-PAN)[**], an isomer of β-PAN, has also been studied[7-13], and found to be very similar to the latter in its chelating properties. More recently, 2-(5-nitro-2-pyridylazo)-1-naphthol (5N-α-PAN) has been introduced. This dye gives extremely sensitive colour changes on chelation and has been suggested as an extractive spectrophotometric reagent for various metals[9].

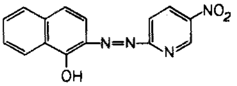
The present paper describes a spectrophotometric method for the determination of trace amounts of copper based on complex formation with 5N-α-PAN. The lack of selectivity of this reagent could be compensated by performing a reasonably selective solvent extraction separation with salicylaldoxime before the analysis.



β-PAN



α-PAN



5N-α-PAN

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[**] This compound was originally described as 4-(2-pyridylazo)-1-naphthol (*p*-PAN)[7]. Independent work, however, has subsequently shown that the dye in fact must have been 2-(2-pyridylazo)-1-naphthol[8-11]. A mixture of the two isomers may be obtained by some methods of synthesis[12].

EXPERIMENTAL

Apparatus

Absorbance spectra were obtained with a Cary 14 recording spectrophotometer. Absorbance measurements at a definite wavelength were made with a Zeiss PMQ II spectrophotometer in 1-cm stoppered cells of glass or fused silica.

Measurements of pH were made with a Metrohm E 396 pH meter equipped with glass and saturated calomel electrodes.

Equilibrations were obtained by agitating the aqueous and organic phases in 100-ml separating funnels with polyethylene stoppers on a mechanical shaker. A constant shaking rate (frequency 150 shakes per min, amplitude 4 cm) was maintained throughout the investigation.

Syntheses

1,2-*Naphthoquinone.* This compound was prepared by the procedure of Fieser and Fieser[14].

2-*Hydrazino*-5-*nitropyridine.* 2-Chloro-5-nitropyridine ("pure" product, Koch-Light Laboratories, Ltd., Colnbrook) was converted to 2-hydrazino-5-nitropyridine by a procedure outlined by Räth[15].

2-(5-*Nitro*-2-*pyridylazo*)-1-*naphthol* (5*N*-α-*PAN*). Some pyridylazo dyestuffs cannot be synthesized by the normal diazo-coupling reaction. However, by the reaction of heterocyclic hydrazine derivatives with 1,2-naphthoquinone in the presence of acid, azo dyes of 1-naphthol are exclusively produced[10,16]. In the present work this method was used for the preparation of 5N-α-PAN, as described by Kawase[9,17].

To a solution containing 4.0 g of 1,2-naphthoquinone in 40 ml of hot acetic acid 3.9 g of 2-hydrazino-5-nitropyridine was added. The resulting mixture was allowed to stand for 1 h. On neutralization with dilute sodium hydroxide solution a precipitate of 5N-α-PAN was formed. The crude dye was isolated by filtration and washed well with water. Unreacted materials were removed by washing successively with small portions of hot ethanol and hot dioxane. The product was recrystallized from dioxane to give brown red crystals (m.p. 245–6° uncorrected; lit.[9] 248°). The dye thus obtained was found by thin-layer chromatography to be homogeneous, and to have spectral characteristics (*vide infra*) identical with those reported earlier[9]. Elemental analysis gave the following results: 61.57% C, 3.47% H, 18.83% N; calc. for $C_{15}H_{10}N_4O_3$: 61.23% C, 3.42% H, 19.04% N.

Reagents

All chemicals were of analytical-reagent grade unless otherwise specified. Deionized water was purified by distillation in an all-glass (Pyrex) still. Dioxane and chloroform (the latter containing 0.6–1.0% ethanol as a stabilizer) were used without further purification.

Standard solutions of copper(II). A stock solution (*ca.* $5.0 \cdot 10^{-3}$ *M*) was prepared by dissolving copper(II) sulphate pentahydrate in water, adding a few drops of concentrated sulphuric acid and diluting to volume; the solution was standardized against EDTA. Freshly made standard solutions of lower concentration were obtained by appropriate dilution as required.

Salicylaldoxime solution. A 10^{-3} *M* solution of the reagent (E. Merck A. G., Darmstadt) in chloroform was stored in a brown glass bottle. When preserved under such conditions salicylaldoxime solutions are stable for at least 3 years.

5N-α-PAN solutions. Solutions of the dye in chloroform and dioxane were employed. Kept away from sunlight when not in use, these remain stable for several months.

Buffer solutions. In the study of absorbance spectra and complex stoichiometry buffers of fixed ionic strength were used. These were made from 0.05 *M* ammonium chloride, the pH being adjusted with sodium hydroxide and the desired ionic strength maintained by addition of potassium chloride[18].

The method of continuous variations

The method of continuous variations—as extended to an extractable species in a two-phase system[19]—was applied, with the experimental techniques of Pilipenko[20]. The ionic strength of the aqueous phase was kept at 0.1, and the pH at equilibrium was 9.3.

RESULTS AND DISCUSSION

Complex formation and solvent extraction

5N-α-PAN is nearly insoluble in water, but soluble in a variety of water-miscible organic solvents, including methanol, ethanol, acetone and dioxane. The dye is more soluble in dioxane than in the other solvents mentioned. For this reason dioxane was chosen as solvent for the reagent in most experiments.

When a solution of 5N-α-PAN in dioxane is added to a copper(II) solution of appropriate pH the orange colour of the dye changes almost instantaneously to a greenish blue because of complex formation. The complex is only slightly soluble in water and forms a colloidal suspension or precipitate, which is readily extracted with organic solvents. Chloroform was chosen because it is denser than water and may be used to extract the copper(II)–salicylaldoxime chelate.

Extraction of the complex may also be performed in another way, *viz.* by shaking an aqueous copper(II) solution with a solution of 5N-α-PAN in chloroform. This procedure is less suitable for analytical purposes, as the time required for establishing equilibrium is longer. It was used, however, in the investigation of absorbance spectra and complex stoichiometry described below.

Choice of pH

The influence of pH on solvent extraction has been studied by Kawase[9], who found that the complex is completely extracted into chloroform from sodium acetate–borax buffered solutions in the pH range 6–9.2. The present work demonstrated that quantitative extraction of copper with 5N-α-PAN could also be obtained in the presence of aqueous ammonia–ammonium chloride buffers at pH 8.7–9.8. A pH of 9.3 was selected for further studies as a matter of convenience.

Absorbance spectra

Absorbance spectra of 5N-α-PAN and its copper(II) complex are reproduced in Fig. 1. The spectrum of the dye itself exhibits two maxima at 367 and 489 nm respectively. This is in accordance with the tendency of α-PAN and its derivatives to absorb light at somewhat longer wavelengths than β-PAN[9,10,16].

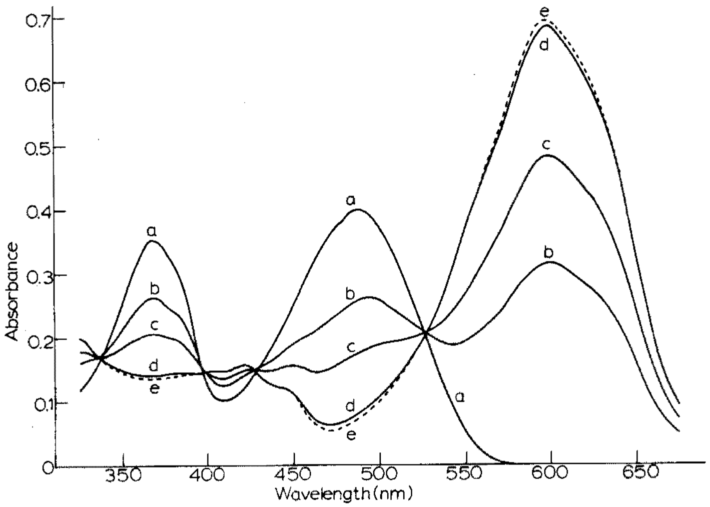

Fig. 1. Absorbance spectra of 5N-α-PAN and its copper(II) complex. (a) $1.6 \cdot 10^{-5}$ *M* 5N-α-PAN in chloroform after equilibration for 30 min with an equal volume of a buffer solution (pH 9.3, $\mu = 0.1$). (b–e) As (a) but with copper present in the aqueous phase: $0.2 \cdot 10^{-5}$ *M* (b), $0.4 \cdot 10^{-5}$ *M* (c), $0.8 \cdot 10^{-5}$ *M* (d), $1.6 \cdot 10^{-5}$ *M* (e). All spectra recorded *vs.* chloroform blank.

On complex formation with copper(II) a large bathochromic shift in the wavelength of maximum absorbance (489 nm) is produced. The shift is 109 nm, as opposed to 95 and 98 nm, respectively, for the corresponding β-PAN and α-PAN complexes[9]. Obviously this feature is an asset to the use of 5N-α-PAN as a colorimetric reagent for copper.

Nature of complex

The absorbance spectra given in Fig. 1 indicate that only one complex is formed between copper(II) and 5N-α-PAN at pH 9.3. The curves suggest a metal-to-ligand ratio of 1:2.

To obtain further information on the stoichiometry of the complex, continuous variation experiments were made. The results of two representative series are presented in Fig. 2. Both plots show a distinct maximum at a mole fraction of copper of 0.33 and clearly prove the formation of a 1:2 chelate.

Effect of experimental variables

It was found that a 4-fold molar excess of 5N-α-PAN over copper in the aqueous phase was sufficient to obtain maximum colour response. However, in experiments leading to the development of the *Analytical procedure* a minimum 10-fold excess of the reagent was employed. The complex was formed within 2 min after mixing of the copper(II), buffer and reagent solutions. As a safeguard a reaction time of 5 min was allowed for.

The complex as well as excess of reagent was rapidly extracted into chloroform in a single pass. Equilibration for 1 min was found to be adequate for quantitative extraction; a further increase in shaking time had no effect on the absorbance caused by a given amount of copper. The absorbance of the extract was then constant

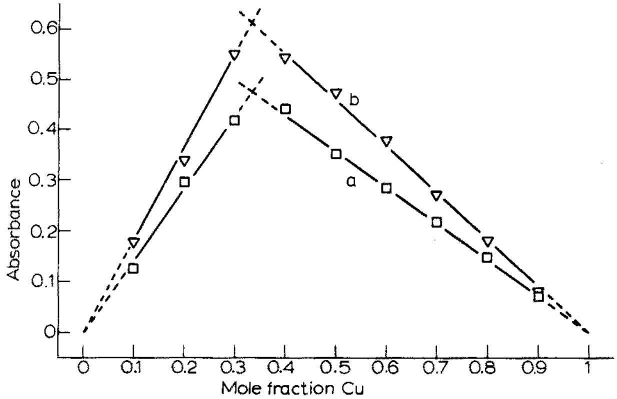

Fig. 2. Continuous variation plots for the copper(II)–5N-α-PAN system. Buffered copper solutions (pH 9.3, $\mu = 0.1$) mixed in various proportions with equimolar solutions of 5N-α-PAN in chloroform to give a total volume of 50 ml, and then equilibrated for 30 min. Organic phases diluted to 50 ml with chloroform and measured spectrophotometrically. Concentration of reactant solutions: $2.0 \cdot 10^{-5}$ *M* (a) and $2.5 \cdot 10^{-5}$ *M* (b). Absorbances measured at 598 nm *vs.* chloroform blanks.

for several hours; readings were conveniently taken after 15–30 min. Normal variations in room temperature did not affect the absorbance.

Beer's law

The molar absorptivity of the copper(II)–5N-α-PAN complex in chloroform is 86,000 at 598 nm, corresponding to a sensitivity index (Sandell) of 0.00074 μg Cu cm^{-2}. Under the conditions of the *Analytical procedure* a practical molar absorptivity of about 80,000 is achieved. Beer's law is obeyed over the entire concentration range studied, *i.e.* $0.5–10 \cdot 10^{-6}$ *M* Cu (31.7–634 μg Cu l^{-1}).

Development of analytical method

In a previous paper[1] the selective extraction of copper with solutions of salicylaldoxime in benzene has been reported. Preliminary experiments showed that chloroform could be used as solvent instead of benzene without any loss in selectivity. Subsequent experiments with 10^{-3} *M* salicylaldoxime in chloroform showed that copper is quantitatively extracted down to a pH of 3.8. At pH 3.2 the extraction is still about 90% complete in one pass.

In the *Analytical procedure* copper(II) is first extracted into chloroform as its salicylaldoxime chelate from an aqueous solution buffered to pH 3–4 with potassium hydrogenphthalate. Copper is then back-extracted with dilute hydrochloric acid containing ammonium chloride, and the aqueous phase is washed with chloroform. The pH is adjusted to 9.3 by adding a calculated amount of sodium hydroxide, thus neutralizing the acid and establishing an ammonia–ammonium ion buffer system. After the addition of 5N-α-PAN, copper is finally re-extracted into chloroform, and the absorbance of the extract is measured at 598 nm in a 1-cm cell.

In this procedure the complexes are partitioned between aqueous and organic phases of approximately equal volumes. By using more favourable volume ratios at the various extraction steps the analytical sensitivity should be substantially increased. Of course a greater sensitivity can also be obtained by using longer cells for the absorbance measurements.

Effect of foreign ions

Although no extensive examination of the effect of foreign ions was undertaken, the influence of some selected ions was studied. Common anions, such as chloride, nitrate, sulphate, and phosphate, did not interfere. The presence of large amounts of complexing agents, *e.g.* citrate, may lead to incomplete extraction of copper by salicylaldoxime.

With regard to cation interference it was found that at least a 500-fold molar excess of nickel(II) over copper could be tolerated. In view of earlier findings[1,2] it is reasonable to assume that lead(II), cobalt(II), manganese(II), zinc(II), cadmium(II), mercury(II), magnesium(II), and aluminium(III) would cause no interference.

Determination of copper in metals

The method was tested by determining traces of copper in high-purity magnesium and cobalt metal. The results obtained are shown in Table I.

TABLE I

ANALYSIS FOR COPPER IN METAL SAMPLES

Material	*% Cu*	
	Reported	*Found*
High-purity Mg	0.0020	0.00203, 0.00204, 0.00206, 0.00204
High-purity Co	0.0035[a]	0.00354, 0.00338

[a] Atomic absorption method.

ANALYTICAL PROCEDURE

Sample preparation

Magnesium. Dissolve 2 g of the sample in 50 ml of hydrochloric acid (1+3) and heat just to boiling. Cool and transfer to an appropriate volumetric flask. Neutralize by dropwise addition of concentrated ammonia solution and dilute to volume with water.

Cobalt. Dissolve a 1-g sample in 8 ml of nitric acid (1+1) and evaporate to complete dryness on a water bath. Dissolve the residue in 10 ml of water plus 1 drop of nitric acid (1+1), transfer to a volumetric flask and make up to the mark with water.

Analysis

Place a 20-ml aliquot of the sample solution, containing up to 12 μg of copper, in a 100-ml separating funnel. Add 5 ml of 0.4 M potassium hydrogenphthalate solution followed by 20 ml of 10^{-3} M salicylaldoxime solution in chloroform and shake vigorously for 2 min. Allow 5 min for the two phases to separate and run off the chloroform layer into a second 100-ml separating funnel. Add to this 20 ml of the stripping solution (0.1 *M* with respect to hydrochloric acid and 0.05 *M* with respect to ammonium chloride), shake for 2 min and discard the organic phase as soon as the layers have settled. Make a 1-min wash extraction with 20 ml of chloroform and discard the latter. Add 5 ml of 0.5 *M* sodium hydroxide solution and swirl the funnel for a few seconds. Then, with swirling, add 1 ml of a $2 \cdot 10^{-3}$ *M* 5N-α-PAN solution in dioxane and let stand for 5 min. Finally add 20 ml of chloroform and shake for 1 min. After 15–30 min drain a portion of the chloroform extract into a 1-cm cell. Measure the absorbance at 598 nm against a blank which has been carried through the same procedure.

Calibration

Prepare sample solutions with known additions of copper and proceed as directed in *Analysis*.

SUMMARY

A highly sensitive spectrophotometric method for the determination of traces of copper with 2-(5-nitro-2-pyridylazo)-1-naphthol (5N-α-PAN) has been developed. At a pH of 3–4 copper(II) is selectively extracted into chloroform as its salicylaldoxime chelate and then stripped into an aqueous acid solution; the pH is adjusted to 9.3, and 5N-α-PAN is added. The 1:2 chelate between copper(II) and the reagent, which promptly precipitates, is extracted into chloroform and measured at 598 nm. The molar absorptivity is 86,000. The application of the method to the analysis of high-purity magnesium and cobalt is described.

RÉSUMÉ

On propose une méthode spectrophotométrique très sensible pour le dosage de traces de cuivre, au moyen de 2-(5-nitro-2-pyridylazo)-1-naphtol (5N-α-PAN). Le cuivre(II), sous forme de son chélate salicylaldoxime, est extrait sélectivement dans le chloroforme, à pH 3–4. Il est ensuite strippé dans une solution aqueuse d'acide, précipité à l'aide de 5N-α-PAN, extrait dans le chloroforme et mesuré à 598 nm (coefficient d'extinction molaire 86,000). Ce dosage peut être appliqué à l'analyse de magnésium et de cobalt de grande pureté.

ZUSAMMENFASSUNG

Es wurde eine hochempfindliche spektrophotometrische Methode für die Bestimmung von Spuren Kupfer mit 2-(5-Nitro-2-pyridylazo)-1-naphthol (5N-α-PAN) entwickelt. Bei einem pH-Wert von 3–4 wird Kupfer(II) selektiv als Salicylaldoxim-Chelat mit Chloroform extrahiert und dann mit einer wässrigen sauren Lösung zurückextrahiert; der pH-Wert wird auf 9.3 eingestellt und darauf 5N-α-PAN hinzugefügt. Das 1:2-Chelat zwischen Kupfer(II) und dem Reagenz, das sofort ausfällt, wird mit Chloroform extrahiert und bei 598 nm gemessen. Der molare dekadische Extinktionskoeffizient ist 86000. Die Anwendung der Methode auf die Analyse von hochreinem Magnesium und Kobalt wird beschrieben.

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EXTRACTION OF COBALT, IRON, INDIUM AND ZINC FROM SEAWATER BY MEANS OF THE TRIFLUOROACETYLACETONE–TOLUENE SYSTEM*

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There is currently an accelerating interest in the development of techniques for the analysis of trace metals in seawater. Much of the recent activity has been engendered by concern over the potential build-up of heavy-metal pollutants in the marine environment, and has been primarily concerned with particulate forms of the metals; fish and adjacent trophic level species are of prime interest. A full understanding of natural cycles and pathways of metals in the sea requires, however, determination of precise and accurate values for dissolved species, and the acquisition of such information has always been hampered by the limited number of techniques available for ultratrace analysis in such matrices. Most of the analytical methods used rely on a more-or-less complex pre-analysis concentration and separation sequence. The latter steps are potentially the major sources of analytical error limiting the overall utility of the data[1]. Two problems in particular in marine trace metal analysis need increased emphasis[1]: qualitative and, ultimately, quantitative chemical speciation of the dissolved fractions, and development of direct analytical methods. A long-range goal might well be deployment of continuous or automated time–series analysis modules; but this is a more immediate requirement for fresh water systems.

Anodic-stripping voltammetry is a very suitable direct (and portable) procedure for a limited range of metals, and observed peak-potential shifts[2] suggest the possibility of at least a simple characterization of the contributing chemical forms. Both neutron activation and atomic spectrometric analysis give total values for a wide range of metals. The former technique is immobile and hence not well suited to monitoring such large-scale dynamic systems as the oceans. Atomic absorption spectrometry has long been used for marine trace metal analysis preceded by a concentration step. More recently, by using discrete sample introduction and non-flame atomization, direct analyses have been reported[3,4].

One further sensitive analytical technique, gas–liquid partition chromatography, has not yet been applied to seawater trace metal analysis, although absolute detection limits in the ng–pg range are obtainable. Since this method requires partition and detection of metals as organo-complexes, analysis must be preceded by a suitable chelation and solvent extraction, and similar treatments may also be used to prepare volatile metal compounds for subsequent mass spectrometric analysis.

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It should be noted that (unlike the preparatory chemistry for most conventional trace analysis methods) concentration of the metal species is not a primary aim. This communication is concerned with the applicability of one such system to the extraction of cobalt, iron, indium and zinc in a seawater matrix.

THE TRIFLUOROACETYLACETONE–TOLUENE SYSTEM

Fluorinated β-diketone chelates have vapor pressures in the range 0.1–1.0 mm, and Al, Be, Cr, Fe and In (in various materials) have been successfully sequestered by the trifluoroacetylacetone ligand in several studies[5–9] for subsequent g.l.c. analysis with an electron-capture detector. Kowalski and Isenhour[10] have reported on the mass spectrometric analysis of a range of metals (including Al, Cr, Cu, Fe, Ni and Pb) with heptafluorodimethyloctanedione chelates, and a study of the lead chelate has been made by Belcher *et al.*[11]. The detection limits for both g.l.c. (with electron-capture detection) and mass spectrometric analysis are of the order of 10^{-12} g μl^{-1} of the metals studied to date; this is the concentration range of many trace metals in seawater[12]. Both techniques are suitable for simultaneous multi-element analysis.

The present work on the extraction of the Co, Fe, In and Zn chelates of trifluoroacetylacetone from a seawater medium—with the ultimate objective of g.l.c. and/or mass spectrometric analysis—was prompted in part by the considerable information available on these complexes. An additional bonus to the marine chemist may well be the favorable chelation with trifluoroacetylacetone of trivalent metals which are, in general, less amenable to analysis by the conventional techniques noted above. For example, the g.l.c. analysis of soluble aluminum in natural waters by the system described here will be reported shortly.

Metal ions with charge (Z) equal to one half the coordination number give coordination-saturated chelates with trifluoroacetylacetone which are readily extracted by non-polar solvents. This is not so for coordination-unsaturated complexes where the coordination number of the central metal ion is greater than twice the charge[13]. These latter unsaturated chelates retain free coordination sites occupied by oxygen-containing groups. Thus a chelate containing coordinated water may be only poorly extracted into non-oxygen-containing solvents of low polarity. In such cases it is possible to obtain a high solubility in the organic phase by displacing the water with an amine group[14]; examples using isobutylamine are considered below.

Many solvents—ketones, esters and (especially) alcohols—quantitatively extract both coordination-saturated and -unsaturated chelates of the type considered here[13]. However, polar solvents with electron affinity which interferes with the electron-capture detection are not suitable for subsequent g.l.c. analysis[15]. The suitability of toluene for g.l.c.–electron-capture analysis has been previously well documented[16] and was therefore selected for this study. Such restrictions on the solvent would not necessarily apply to mass spectrometric detection.

EXPERIMENTAL

Reagents

Trifluoroacetylacetone and isobutylamine were obtained from Columbia

Organic Chemicals Company. The former was distilled and the fraction boiling from 106 to 107° was collected and stored at 5°. Toluene was Mallinckrodt nanograde.

Extraction procedure

A seawater sample (pH 7.84) was adjusted to give various pH sub-samples with sodium hydroxide and hydrochloric acid; 15-ml aliquots of each sub-sample were added to 125-ml separatory funnels (with teflon stopcocks) and treated with 2 ml of ^{114m}In, ^{59}Fe, ^{60}Co, or ^{65}Zn solution. Each labelled seawater sample was then thoroughly mixed and 2-ml portions were withdrawn for counting. The reagent solution (15 ml of toluene–trifluoroacetylacetone (0.1 *M*), or toluene–trifluoroacetylacetone (0.1 *M*)–isobutylamine (0.4 *M*)) was added and the mixture was mechanically shaken for 10 min (60 min for indium). After equilibrium, the mixture was allowed to stand until separation was complete. A further 2 ml from each phase was then counted, and the values for % extraction of the metal ions were calculated. The pH of the aqueous phase after extraction was taken to be the equilibrium pH (the pH at which the rates of ligand dissociation and association are equal). Various amounts of seawater, and different equilibrium times, were also used to check the extraction efficiency as a function of aqueous/organic volume ratio and the equilibrium time. The effect of the concentration of isobutylamine on the extraction of zinc was also studied.

RESULTS

Indium

Over the pH range 6.3–10, indium was 99.5% extracted with an equal volume

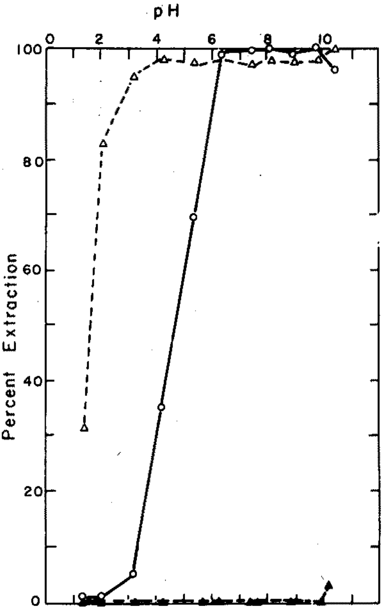


Fig. 1. Effect of pH on extractability of iron, indium, and zinc from seawater with toluene–trifluoroacetylacetone (0.1 *M*); phase ratio 1:1. (---) Fe; (—·—) Zn; (—) In.

of toluene–trifluoroacetylacetone (0.1 *M*) solution in a single extraction within 5 min (Figs. 1 and 2), and 90% of the indium present was removed with an aqueous/organic volume ratio of 20 (Fig. 3).

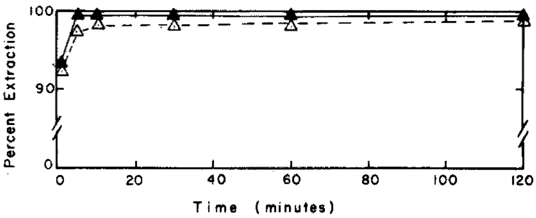


Fig. 2. Effect of time on extraction of iron and indium from seawater with toluene–trifluoroacetylacetone (0.1 *M*); phase ratio 1:1. (---) Fe; (—) In.

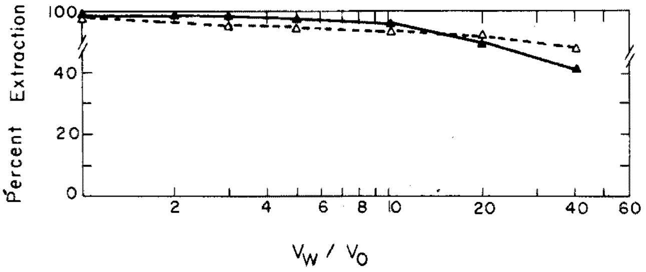


Fig. 3. Efficiency of extraction of iron and indium from seawater with toluene–trifluoroacetylacetone (0.1 *M*) as a function of water/organic phase ratio. (---) Fe; (—) In.

Iron

Iron was quantitatively extracted (Fig. 1) with toluene–trifluoroacetylacetone (0.1 *M*) in a single (1:1) extraction over the pH range 4–10, and equilibrium was reached within 10 min (Fig. 2). An 88.5% extraction was obtained with a phase ratio of 40 (Fig. 3).

Zinc

No zinc (or only a trace) was removed from seawater at any pH with toluene–

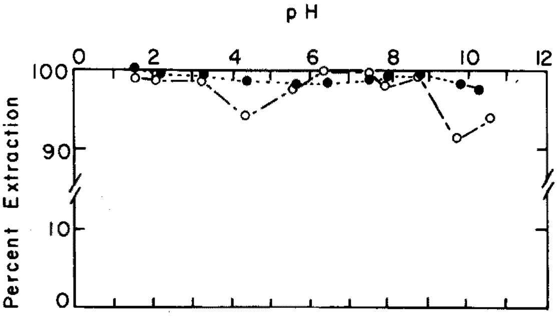


Fig. 4. Effect of pH on extractability of zinc and cobalt from seawater with toluene–trifluoroacetylacetone (0.1 *M*)–isobutylamine (0.4 *M*); phase ratio 1:1. (——·——) Zn; (...) Co.

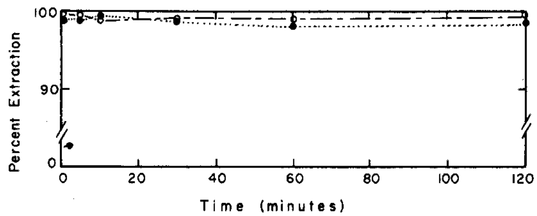
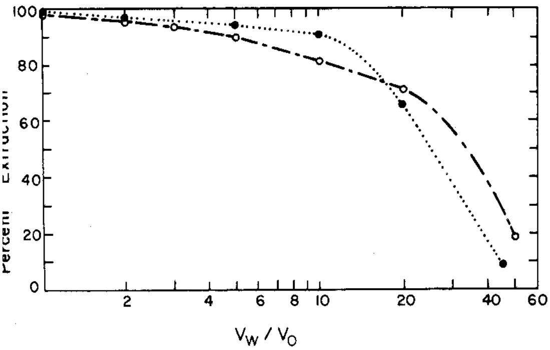


Fig. 5. Effect of time on extraction of cobalt and zinc from seawater with toluene–trifluoroacetylacetone (0.1 M)–isobutylamine (0.4 M); phase ratio 1:1. (——-) Zn; (...) Co.

trifluoroacetylacetone (0.1 M) (Fig. 1); a result found to be not attributable to the presence of the major divalent ions, *e.g.* magnesium. Zinc was, however, quantitatively and instantaneously extracted from seawater over the pH range studied with an equal volume of toluene–trifluoroacetylacetone (0.1 M)–isobutylamine (0.4 M) (Figs. 4 and 5). Lesser extraction efficiencies of the metal ion were recorded whenever a trace of white precipitate was observed at the interface of the two phases (Fig. 4). Foams existed at the interface of all samples, but the extraction efficiency was not affected with volume ratio up to 50. Extractability decreased greatly if the aqueous/organic volume ratio was greater than 10 (Fig. 6), and the organic phase was completely foamy if the phase ratio exceeded 50. The zinc extraction was independent of extraction time.

Cobalt

This ion also could not be extracted from seawater with toluene–trifluoroacetylacetone (0.1 M) alone, but the characteristics of cobalt extraction with toluene–trifluoroacetylacetone (0.1 M)–isobutylamine (0.4 M) were quite similar to those for zinc, except that precipitation did not interfere (Figs. 4, 5 and 6). The distribution of the cobalt chelate was independent of pH and extraction time over the range studied. The amounts of isobutylamine needed for the extraction of both cobalt and zinc were found to be very critical; for a 15-ml seawater sample, for example, at least 0.2



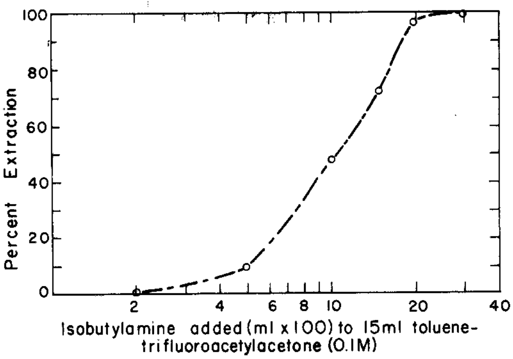


Fig. 6. Efficiency of extraction of zinc and cobalt from seawater with toluene–trifluoroacetylacetone (0.1 M)–isobutylamine (0.4 M) as a function of water/organic phase ratio. (——-) Zn; (...) Co.

Fig. 7. Effect of the concentration of isobutylamine on the extractability of zinc from seawater with 15 ml of toluene–trifluoroacetylacetone (0.1 M); phase ratio 1:1.

ml was needed for 15 ml of toluene–trifluoroacetylacetone (0.1 *M*) solution to obtain a quantitative extraction (Fig. 7).

In all cases the equilibrium pH was invariably lower than the initial pH value, owing to the replacement of hydrogen ion by the metal ions extracted, and to the dissociation of the unchelated trifluoroacetylacetone.

DISCUSSION

The following are the major factors which govern the extraction of metal ions from seawater.

(*a*) The initial pH of the aqueous solution directly affects the chelation reaction

$$M^{n+} + nHR \rightleftharpoons MR_n + nH^+; \quad K = \frac{(MR_n)(H^+)^n}{(M^{n+})(HR)^n} \tag{1}$$

where M^{n+} is the metal ion of interest and HR the reagent; in this case, trifluoroacetylacetone. Equation (1) shows the pH dependence of the chelate formation (see Fig. 1); trifluoroacetylacetone is acidic, and the formation of a chelate is accompanied by the displacement of hydrogen ions. The time to reach equilibrium is largely limited by the rate of chelate formation, which, in turn, depends upon the concentration of the trifluoroacetylacetone anion. The latter is influenced by the pH of the aqueous solution. Thus

$$HR \rightleftharpoons H^+ + R^-; \; K_a = \frac{(H^+)(R^-)}{(HR)} \tag{2}$$

where K_a is the acid dissociation constant of trifluoroacetylacetone ($5 \cdot 10^{-7}$ from Reid and Calvin[17]). No attempt has been made to correct this value to a "seawater medium" scale (the ionic strength of seawater is *ca.* 0.7).

(*b*) Extraction time is critical, since the time for the system to reach equilibrium is governed by the rate of chelate formation.

(*c*) The trifluoroacetylacetone concentration is important. Since the total concentration of the extractable fraction of trace elements in seawater is very low, a minute amount of trifluoroacetylacetone (about 10^{-4} *M*) would theoretically suffice for a quantitative extraction, but this variable is eliminated by employing a large excess. The approximate resultant concentration of trifluoroacetylacetone in the aqueous phase is about 0.06 *M* (based on $K_d = (HR)_o/(HR)_w = 0.57$, where o and w refer to the organic and aqueous phases, respectively[18]). The concentration of trifluoroacetylacetone can therefore be regarded as constant during the extraction. Additionally, use of a high concentration of trifluoroacetylacetone shortens the equilibrium time and permits the extraction to be carried out in a more acidic solution than usual.

(*d*) Ions in seawater act as salting-out agents, and one important aspect of this is the binding of water molecules by cations; water is bound as a shell of oriented dipoles around the metal ions, thus depleting their use as a solvent. If the metal ions of interest and the trifluoroacetylacetone are considered as definite though transient ion pairs, they are brought together by electrostatic attraction, and the association of the pairs will be greater the lower the dielectric constant of the solvent. One of the effects of the ions in seawater is to decrease the dielectric constant[19].

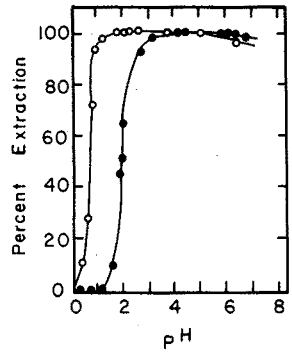


Fig. 8. Effect of pH on the extraction of iron and indium from perchlorate solution of 0.1 ionic strength with benzene–trifluoroacetylacetone (0.25 *M*); phase ratio 5:1. (○) $8 \cdot 10^{-3}$ *M* Fe; (●) $8 \cdot 10^{-3}$ *M* In (from Morie and Sweet[20,21]).

Iron and indium evidently form coordination-saturated chelates with trifluoroacetylacetone and are extracted excellently into toluene from seawater. Zinc and cobalt, however, are extracted poorly by toluene, since their chelates contain two molecules of water. Displacement of the water molecules by isobutylamine explains the data obtained (Figs. 5–8), and these results are in accord with the conclusions of Alimarin and Zolotov[13]. A poor extraction of all metals with toluene–trifluoroacetylacetone (0.1 *M*) occurs at low pH. This can be attributed to a decreased dissociation of the ligand in the presence of a high concentration of hydrogen ion in the aqueous solution, as discussed above. The high extraction efficiencies of cobalt and zinc over a wide pH range may be partially due to the addition of isobutylamine, which increases the pH of the aqueous phase to a value greater than 10.

It is of interest to compare the curves for iron and indium of Fig. 1 with the corresponding curves of Fig. 8 (from Morie and Sweet[20,21]). The curves for iron and indium determined in this study were less steep and were shifted toward higher pH values; one pH unit higher for iron, two units for indium. This phenomenon may be attributed to the presence of a high concentration of halogen ions in seawater, despite the difference in ionic strength of the two media. The difference in degree of the metal hydrolysis in these media is considered to be negligible, and the halogen ions form complexes with these ions. Steinbach and Freiser[22] have derived the following equation for the effects of complex formation on the chelate distribution between organic and aqueous phases:

$$D = \frac{[P_c - D]}{1 + K_x(X^-)} \cdot \frac{[K_a^n(HR)_w^n K_f]}{(H^+)^n} \tag{3}$$

where

$$M^{n+} + X^- \rightleftharpoons MX^{(n-1)}; \quad K_x = \frac{(MX^{(n-1)})}{(M^{n+})(X^-)} \tag{4}$$

$$M^{n+} + nR^- \rightleftharpoons MR_n; \quad K_f = \frac{(MR_n)}{(M^{n+})(R^-)^n} \tag{5}$$

and D is the ratio of the stoichiometric metal concentrations in the two phases; P_c the partition coefficient of the chelate; (X^-) the halogen or hydroxyl ion concentration (other minor anions in seawater may be neglected). Equation (3) shows that the slope of the resultant extraction curve decreases with increasing (X^-) and pH, and that the difference in (X^-) of the two media at any pH is equal to the halogen ion concentration in seawater. For each medium, when D is differentiated with respect to (H^+), the $K_x(X^-)$ term is removed. The curve is thus shifted toward higher pH values without a change of shape, depending upon the magnitude of $K_x(X^-)$. Variations in $(HR)_w$ need not be considered here. Since (HR) is in excess, such differences should not affect the result. These considerations should suffice to explain the change of slope and shift of curves of iron and indium of Figs. 1 and 8.

The composition of the seawater medium influences the extraction characteristics in other ways also. Thus, the equilibrium time for complete extraction of In–trifluoroacetylacetone reported by Morie and Sweet (1966)[20] is more than 1 h, whereas in this study (Fig. 2), total extraction is possible in less than 5 min. Moreover, zinc and cobalt may be extracted with toluene–trifluoroacetylacetone (0.1 *M*)–isobutylamine (0.4 *M*) over a much wider pH range (Fig. 4) than that reported by Scribner and Kotecki[14]. It may be concluded that seawater (ionic strength 0.7) is a better medium for the solvent extraction of these metal chelates than would be the case from fresh water samples.

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SUMMARY

Iron, indium, cobalt and zinc may be completely and rapidly extracted in a single extraction with an equal volume of toluene–trifluoroacetylacetone (0.1 *M*) for Fe and In, and toluene–trifluoroacetylacetone (0.1 *M*)–isobutylamine (0.4 *M*) for Co and Zn. A 90% extraction of indium is obtained with an aqueous/organic volume ratio of 20, and a 88.5% extraction for iron with a volume ratio of 40. There is a deviation of the iron and indium extraction curves from seawater compared with the theoretical trivalent metal curves; this is attributed to the high concentration of halogen ions in seawater, which makes seawater a superior medium for solvent extraction.

RÉSUMÉ

Fer, indium, cobalt et zinc peuvent être extraits totalement et rapidement avec une simple extraction toluène–trifluoroacétylacétone pour Fe et In, et toluène–trifluoroacétylacétone–isobutylamine pour Co et Zn. On observe une déviation entre les courbes d'extraction Fe et In d'une eau de mer, comparées aux courbes théoriques de ces métaux trivalents. Ceci peut être attribué à la forte concentration en halogénures de l'eau de mer, et constitue un avantage pour une extraction dans un solvant.

ZUSAMMENFASSUNG

Eisen, Indium, Kobalt und Zink können vollständig und schnell durch eine

einzige Extraktion extrahiert werden. Für Fe und In wird ein gleiches Volumen Toluol–Trifluoracetylaceton (0.1 *M*) und für Co und Zn Toluol–Trifluoracetylaceton (0.1 *M*)–Isobutylamin (0.4 *M*) verwendet. Bei einem Volumenverhältnis wässrige/organische Phase von 20 wird eine 90 %ige Extraktion von Indium, bei einem Volumenverhältnis von 40 eine 88.5 %ige Extraktion von Eisen erzielt. Bei den Extraktionskurven von Eisen und Indium aus Meerwasser tritt eine Abweichung von den theoretischen Kurven für dreiwertige Metalle auf. Dies wird auf die hohe Konzentration von Halogenidionen in Meerwasser zurückgeführt, das ein vorzügliches Medium für die Extraktion ist.

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CATION EXCHANGE IN ACETIC ACID SOLUTIONS

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Studies on the behaviour of elements on cation-exchange resins in formic acid–water[1] and formic acid–water–dioxan[2] systems have been recently reported. Selectivity coefficients[3] *vs.* solvent composition studies for alkali metal exchanges with barium in acetic acid–water mixture have also been carried out. Useful data on the ion selectivities for cation exchangers in non-aqueous and mixed solvent systems are also available[4]. However, so far no systematic study on the behaviour of the elements on cation-exchange resins in acetic acid–water systems has been published.

The present paper deals with the adsorbabilities of the elements on a strongly acidic cation-exchange resin as a function of the acetic acid concentration in water–acetic acid solutions. The usefulness of the adsorption functions is shown by some interesting separations.

EXPERIMENTAL

Analytical-grade, sulphonated polystyrene–divinyl benzene cation-exchange resin in the hydrogen form (Bio-Rad AG 50W-X8) was used. It was conditioned[5] before use and dried by simple heating at 100°.

Both column and batch techniques were applied for measuring adsorbabilities. These are expressed as weight distribution coefficients K_D (amount of ion per g of dry resin/amount of ion per ml solution).

For the determination of small K_D values (< 10) column chromatography was used. The K_D values are then given by the following expression:

$$K_D = \rho\left(\frac{V_{max}}{V} - i\right) \tag{1}$$

where ρ = specific volume of the resin (ml per g dry resin);
i = void fraction of the column;
V_{max} = peak elution volume (ml);
V = total volume of the column (ml).

Measurement of ρ, the specific volume, was done as reported earlier[6]. In Fig. 1 the specific volume is given as a function of the acetic acid molarity. As is evident from Fig. 1, the specific volume remains practically unchanged up to 8 M acetic acid but decreases thereafter. The void fraction i was taken from Rieman and Walton[5] as being 0.379.

When batch experiments were performed, weighed amounts of dry resin

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* Research associate of the N.F.W.O.

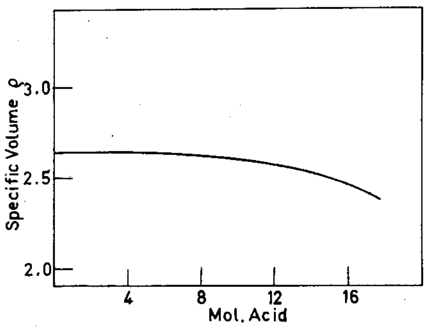

Fig. 1. Specific volume *vs.* acetic acid molarity.

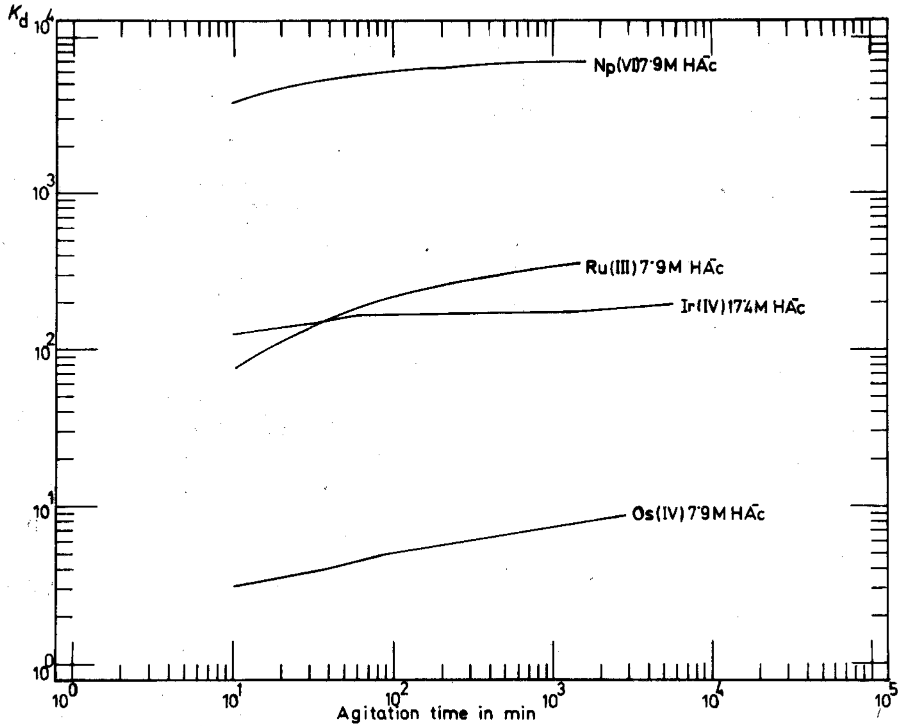

Fig. 2. K_d *versus* time.

were shaken with known volumes of the solution containing the exchangeable ion until equilibrium was attained. After the resin had been filtered off, the concentration of the ion in the liquid phase was determined. The amount of ion originally added to the liquid phase was taken into account and the distribution between liquid and solid phase was then calculated. In all experiments the amount of exchangeable ion was not allowed to exceed 1% of the total exchange capacity (5 meq. g^{-1} of dry resin). The acetic acid molarities varied from 1 *M* to 17.4 *M*. All experiments were carried out at a constant temperature of 25°. A shaking time of 15 h was found to be sufficient to obtain equilibrium. In some cases, where equilibrium was not attained even after this time, K_D values as a function of agitation time are given (Fig. 2).

Analytical methods

Most of the analyses of the liquid phase were done radiometrically. A well-type NaI(Tl) detector was used for integral counting of γ-emitting nuclides. In the presence of more than one tracer or in the analysis of mother–daughter pairs, Ge(Li) or NaI(Tl) γ-spectrometry was used for identification and measurements. In the case of transient equilibria (^{99}Mo–^{99m}Tc, ^{109}Pd–^{109m}Ag, ^{115}Cd–^{115m}In, ^{113}Sn–^{113m}In) the counting was done after the establishment of the mother–daughter equilibrium according to the relation:

$$t_{\mathrm{eq.}} = \frac{1}{\lambda_1 - \lambda_2} \ln \frac{\lambda_1}{\lambda_2} \tag{2}$$

where λ_1 and λ_2 are the decay constants of the mother and daughter, respectively. The measurements in the case of the ^{210}Pb isotope, which is a low-energy γ-emitter (46.5 keV), were done by means of a low-energy photon detector (LEPD). Liquid scintillation counting was preferred for the β-emitting ^{45}Ca isotope.

Most of the tracers were obtained by neutron irradiation of the appropriate target materials in the Thetis reactor in Ghent at a flux of 10^{12} n cm^{-2} s^{-1}. Some long-lived isotopes, requiring a higher flux, were produced in the BR-2 reactor in Mol (10^{14} n cm^{-2} s^{-1}).

The tracers ^{210}Pb–^{210}Bi were obtained as a carrier-free solution from U.K.A.E.A. (Amersham). The ^{210}Bi was separated from ^{210}Pb by anion exchange in nitric acid medium[7].

The $^{101+102+102m}$Rh tracer was obtained from François[8] who prepared it by 18-MeV deuteron bombardment of natural ruthenium.

Information regarding the preparation of tracer solutions after irradiation either in the BR-2 or Thetis reactor is given in Table I. The first column gives the element with its oxidation state in the final tracer solution, followed by the target compound in the second one. The third column gives the isotope measured, whereas the mode of dissolution of the irradiated compound is listed in the fourth. If in the fourth column more than one solvent is mentioned it is obvious that the target compound was not soluble directly in acetic acid. Hence it was taken up, evaporated to dryness or near dryness and redissolved in one or more solvents in the order mentioned. The final solution was filtered wherever necessary.

The ^{210}Bi tracer was obtained by evaporating the 0.25 *M* nitric acid eluate to dryness and dissolving the residue in acetic acid. In the case of rhodium the hydrochloric acid solution was evaporated under an i.r. lamp and redissolved in acetic acid.

Titanium and vanadium were measured spectrophotometrically by the hydrogen peroxide method, as no adequate radioisotope was available. Titanium sponge was dissolved in hydrochloric acid and oxidized by adding a few drops of nitric acid. The solution was then completely evaporated to dryness and taken up in acetic acid. Vanadium(III) solution was prepared by dissolving V_2O_3 in hydrochloric acid.

Measurements of lithium and magnesium were done by atomic absorption spectrophotometry. In both cases the carbonates were directly soluble in acetic acid.

TABLE I

PREPARATION AND DISSOLUTION OF RADIOACTIVE TRACERS

Element + oxidation state	*Target compound*	*Isotope measured*	*Mode of dissolution*	*Element + oxidation state*	*Target compound*	*Isotope measured*	*Mode of dissolution*
Na(I)	Na_2CO_3	^{24}Na	HAc	Ag(I)	$AgNO_3$	^{110m}Ag	HAc
Mg(II)	$MgCO_3$	^{27}Mg	HAc	Cd(II)	CdO	^{115}Cd→ ^{115m}In	HAc
PO_4^{3-}	$(NH_4)_2HPO_4$	^{32}P	HAc	In(III)	In_2O_3	^{116m}In	HCl; HAc
Cl^-	NH_4Cl	^{38}Cl	HAc	Sn(IV)	Sn metal	^{113}Sn→ ^{113m}In	HCl; HAc[f]
K(I)	K_2CO_3	^{42}K	HAc				
Sc(III)	Sc_2O_3	^{46}Sc	HNO_3; HAc	Sb(III)	Sb_2O_3	^{122}Sb	HCl; HAc
Cr(III)	$Cr(NO_3)_3 \cdot 9H_2O$	^{51}Cr	HNO_3 + HF; HAc[a]	Sb(V)	Sb_2O_3	^{122}Sb	A.R.; HAc
			HAc	Te(IV)	TeO_2	^{127m}Te	HNO_3; HAc
Cr(VI)	K_2CrO_4	^{51}Cr	HAc	I^-	NH_4I	^{128}I	HAc
Fe(III)	Fe sponge	^{59}Fe	HCl + H_2O_2; HAc[b]	Ba(II)	$BaCO_3$	^{139}Ba→ ^{140}La	HAc
Co(II)	Co_2O_3	^{60}Co	HNO_3; HAc	La(III)	La_2O_3	^{140}La	HNO_3; HAc
Ni(II)	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4aq.$	^{65}Ni	HAc	Eu(III)	Eu_2O_3	^{152m}Eu	HNO_3; HAc
Cu(II)	CuO	^{64}Cu	HNO_3; HAc	Lu(III)	Lu_2O_3	^{177}Lu	HNO_3; HAc
Zn(II)	ZnO	^{65}Zn	HNO_3; HAc	Hf(IV)	HfO_2	^{180m}Hf	HF; HAc[d]
Ga(III)	Ga_2O_3	^{72}Ga	HF; HNO_3; HAc	Ta(V)	Ta_2O_5	^{182}Ta	HF; H_3BO_3; HAc[g]
Ge(IV)	GeO_2	^{77}Ge	HCl + HF; HAc[c]	W(VI)	WO_3	^{187}W	NH_4OH; HAc

As(III)	As_2O_3	^{76}As	NH_4OH; HAc	Re(VII)	NH_4ReO_4	^{188}Re	HAc
As(V)	As_2O_3	^{76}As	NH_4OH; A.R.; HAc	Os(IV)	$(NH_4)_2OsCl_6$	^{193}Os	HAc
Se(IV)	SeO_2	^{75}Se	HNO_3; HAc	Ir(IV)	$(NH_4)_2IrCl_6$	^{194}Ir	HAc
Br^-	NH_4Br	^{82}Br	HAc	Pt(IV)	Pt metal	^{197}Pt	A.R.; HCl; HAc
Rb(I)	RbCl	^{86}Rb	HAc	Au(III)	H $AuCl_4$ + aq. Au metal[h]	^{198}Au	A.R.; HCl; HAc
Sr(II)	$SrCO_3$	^{89}Sr	HAc				
Y(III)	Y_2O_3	^{90}Y	HCl; HAc	Hg(II)	HgO	^{197}Hg	HNO_3; HAc
Zr(IV)	ZrO_2	^{97}Zr	HF; HAc[d]	Tl(III)	Tl_2O_3	^{204}Tl	HNO_3; HAc
Mo(VI)	$(NH_4)_2Mo_7O_{24} \cdot 4aq.$	$^{99}Mo \rightarrow$ ^{99m}Tc	HAc	Pa(V)	$Th(NO_3)_4$	^{233}Pa	HAc
Tc(VII)	$(NH_4)_2Mo_7O_{24} \cdot 4aq.$	^{99m}Tc	[e]				
Ru(III)	$(NH_4)_2Ru(H_2O)Cl_5$	^{105}Ru	HAc				
Pd(II)	$PdCl_2$	$^{109}Pd \rightarrow$ ^{109m}Ag	HBr; HAc	Np(VI)	$UO_2(Ac)_2$	^{239}Np	HAc

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[a] Probably $Cr(NO_3)_3 \cdot 9H_2O$ was partly decomposed during irradiation and therefore it could not be dissolved directly in HAc. It was first dissolved in HNO_3 with a few drops of HF followed by HAc after evaporating to dryness.

[b] The ^{59}Fe was purified from ^{54}Mn, formed by the reaction $^{54}Fe(n,p)^{54}Mn$, by anion exchange in HCl medium[9].

[c] With a few drops of HF.

[d] Final HF concentration 10^{-2} *M*.

[e] The ^{99m}Tc was separated from the Mo matrix on an anion-exchange column[10]. The Tc eluate (4 *M* HNO_3) was evaporated to dryness and the residue taken up in glacial acetic acid.

[f] The Sn tracer was purified from ^{125}Sb, formed by the reaction $^{124}Sn(n,\gamma,\beta^-)^{125}Sb$, by spontaneous deposition of Sb on Fe foil[11]. The residual solution was taken up in a large volume of acetic acid.

[g] The HF solution was treated with excess H_3BO_3 to volatilize the fluoride as BF_3.

[h] For separation of gold from Cu and Ag, the metal was irradiated.

ADSORBABILITIES

In the following paragraphs a short description of the variation of adsorbabilities with the acetic acid concentration is given groupwise. Wherever the adsorbability is very high and the activity in the liquid phase falls below the limit of precise measurement, the lower limit of K_D was calculated as described by Currie[12].

Alkali metals

In all the cases the K_D values first show a slight decrease with increase of acetic acid molarity. After reaching a minimum they increase first slowly and then change rapidly beyond 13 M acetic acid. Over the whole molarity range the K_D values follow the order Li > Na > K > Rb > Cs (Fig. 3).

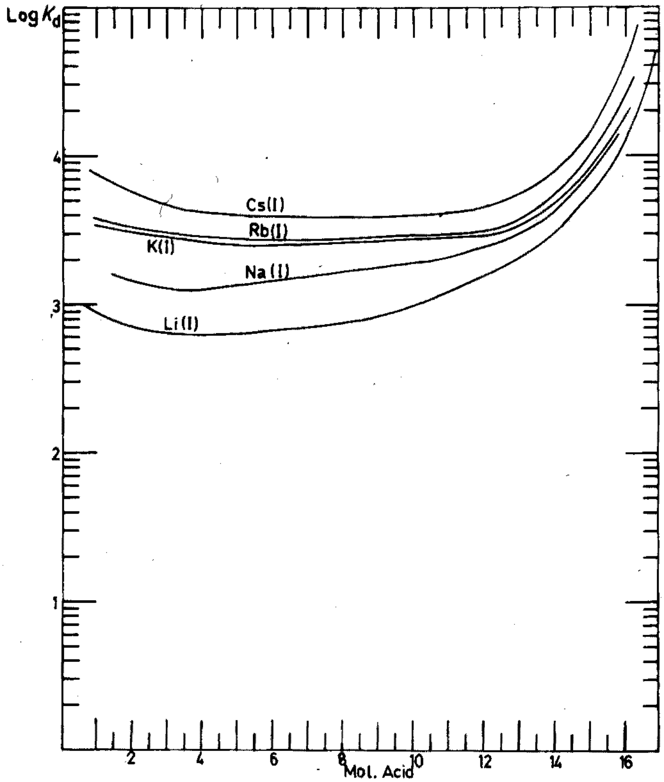

Fig. 3. Adsorption curves for Li(I), Na(I), K(I), Rb(I) and Cs(I).

Alkaline earths

As mentioned earlier, the analysis for magnesium was done by atomic absorption spectrophotometry. Because of the irreproducibility of the results, the behaviour of magnesium cannot be given with certainty. Calcium, strontium and barium show strong adsorption.

For barium it is only possible to give a lower limit. The K_D values for strontium could be calculated for three acetic acid molarities below 6 M, after which it was only possible to give a lower limit. The K_D value could be calculated only at 1.3 M acetic acid for calcium and at higher concentrations only a lower limit can be given. However, these values follow the order Ca > Sr > Ba (Fig. 4).

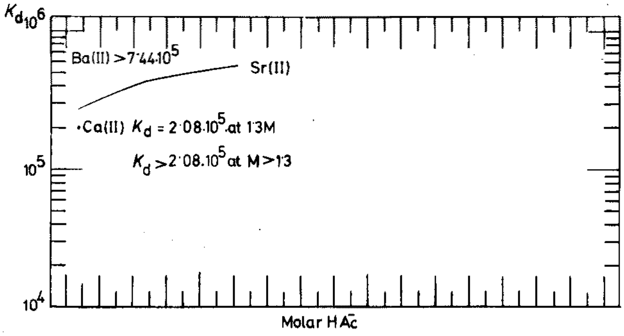

Fig. 4. Adsorption curves for Ba(II), Sr(II) and Ca(II).

Scandium(III), yttrium(III) and rare earths

These elements show a very strong adsorption. In the cases of scandium and yttrium the only possibility is to give a lower limit for the K_D values. The K_D values for lanthanum are of the order of 10^5 and show a slight decrease with increase of the acetic acid molarity beyond 10 M.

Titanium(IV), zirconium(IV) and hafnium(IV)

The K_D of titanium(IV), starting with a value of the order of $2 \cdot 10^3$ at 0.5 M acetic acid, shows a gradual increase and beyond 9 M it is only possible to give the limiting value $K_D > 6.1 \cdot 10^3$. Zirconium was directly eluted in 3 and 13 M acetic acid, the elution yields being not quantitative. Hafnium showed stronger adsorption over the whole molarity range ($K_D > 1.3 \cdot 10^4$).

Vanadium(III) and (IV), tantalum (V) and protactinium(V)

For both vanadium(III) and (IV) only a lower limit value of $K_D > 3 \cdot 10^3$ could be calculated. Tantalum(V) showed almost constant adsorption ($K_D \approx 40$) up to about 10 M acetic acid, beyond which K_D gradually increased, reaching a value of about $3.0 \cdot 10^2$. Irreproducible results were obtained for protactinium, probably because of its tendency to deposit on the walls of glass vessels[13]. The observed K_D values were of the order of $2 \cdot 10^3$.

Chromium(III) and (VI), molybdenum(VI), tungsten(VI) and uranium(VI)

Chromium(III) shows a strong gradually increasing adsorption with a K_D value ranging from $1 \cdot 10^3$ at 1.3 M acetic acid up to $K_D > 1.0 \cdot 10^5$ at 17.4 M acetic acid. Chromium(VI) is directly eluted in 1.025 M acetic acid giving $K_D = 0.5$, while in glacial acetic acid the elution is not possible because of the appearance of a green deposit at the top of column; obviously chromate is reduced to chromium(III). Molybdenum(VI) gives a moderate constant adsorption ($K_D \approx 25$) up to 5 M. For higher molarities it shows gradually increasing adsorbabilities, K_D reaching 270 at 13.4 M acetic acid. At 17.12 M, $K_D = 5 \cdot 10^3$, but at this stage the resin becomes coloured (light blue colour) indicating a reduction to molybdenum blue. Tungsten(VI) is directly eluted over the whole range of acetic acid concentrations. However, the elutions are not quantitative, this effect being more pronounced at higher molarities. Uranium(VI) appears to be strongly adsorbed, as even after very large elution volumes it remains at the top of the column. This was noticed by the deep red colour caused by the reaction between the uranyl ion and potassium hexacyanoferrate(II).

Manganese(II), technetium(VII), rhenium(VII) and neptunium(VI)

Manganese(II) is very strongly adsorbed over the whole range of acetic acid molarities. Adsorption appears to be constant with K_D of the order of $2.1 \cdot 10^5$.

Technetium is directly eluted over the whole range of acetic acid concentration ($K_D < 2$).

When batch experiments were done with neptunium(VI), equilibrium was not reached even after 40 h of agitation. A study of K_D *vs.* time is given in Fig. 2. Rhenium could be directly eluted ($K_D < 1$) but a large fraction of activity was left in the column (4% in 2.9 *M* and 7% in glacial acetic acid).

Iron(III), ruthenium(III) and osmium(IV)

For iron(III), the K_D value indicates a sharp decrease in adsorbability for acetic acid concentrations above 15 *M*, falling from $4.9 \cdot 10^4$ at 16.05 *M* to $2.3 \cdot 10^2$ at 17.09 *M* and being directly eluted at 17.4 *M* acetic acid. Below 15.8 *M*, it is only possible to give a lower limit of the K_D value $> 1.3 \cdot 10^5$. Batch experiments for both ruthenium(III) and osmium(IV) indicated that equilibrium is not reached even after 48 h. K_D values as a function of agitation time are given in Fig. 2.

Cobalt(II), rhodium(III) and iridium(IV)

Cobalt(II) is adsorbed very strongly over the whole molarity range. Only a lower limit for the adsorbability could be calculated ($K_D > 1.3 \cdot 10^6$).

Elution studies of iridium(IV) in two acetic acid molarities (3.09 *M* and 17.4 *M*) showed that though an elution peak could be obtained directly, a large percentage of activity was left in the column (7% in 3.09 *M* and 34% in 17.4 *M*). A study of K_D *vs.* time in glacial acetic acid showed that equilibrium was not obtained even after 96 h. A similar study in 7.9 *M* acetic acid indicated no change of the K_D value with time, giving a constant K_D of 9.3. For rhodium(III) the K_D values varied with the agitation time (Fig. 2).

Nickel(II), palladium(II) and platinum(IV)

Nickel(II) is strongly adsorbed from all acetic acid molarities, the K_D values having a constant value of $3.1 \cdot 10^4$ up to 9 *M* and then increasing to $5.4 \cdot 10^4$ at 13.5 *M* beyond which it is only possible to give a lower limit ($K_D > 5.6 \cdot 10^4$).

Both palladium(II) and platinum(IV) are directly eluted from the column but the elution yields are not quantitative, especially at higher acid molarities.

Copper(II), silver(I) and gold(III)

Copper(II) is very strongly adsorbed from all acetic acid concentrations; it is only possible to give a lower limit for $K_D > 2.7 \cdot 10^5$. Silver(I) gives gradually increasing K_D values between $4.43 \cdot 10^3$ at 1.4 *M* and $5.98 \cdot 10^4$ at 14.8 *M* acetic acid.

Agitation for long duration (4 or 5 days) showed that gold(III) is partially reduced by the resin (the resin as well as the supernatant liquid developed a light purple colour).

It should be mentioned that a gold solution itself is not very stable at higher acetic acid molarity. However, gold from freshly prepared solutions was directly and quantitatively eluted over the whole molarity range ($K_D < 2$).

Zinc(II), cadmium(II) and mercury(II)

Both elements, zinc(II) and cadmium(II) are very strongly adsorbed. Mercury(II) as well shows a fairly strong adsorption. The K_D values show a decrease starting from *ca.* $3 \cdot 10^3$ at 1 *M* to *ca.* $2 \cdot 10^2$ at 15 *M* acetic acid. Above 15 *M* an increase of K_D values was observed.

Gallium(III), indium(III) and thallium(III)

Gallium(III) shows a very strong adsorption. Only a lower limit for the K_D value can be given ($K_D > 2.2 \cdot 10^5$). Thallium(III) gives irreproducible results, probably because of the reduction of thallium(III) to thallium(I). The K_D values were found to be of the order of 10^3. Indium(III) behaves like iron(III) up to 15 *M* acetic acid. At higher molarities the adsorption function rapidly decreases.

Germanium(IV), tin(IV) and lead(II)

Starting from $K_D \approx 50$, the adsorbability of germanium(IV) shows a gradual increase, K_D approaching *ca.* 200 at 17 *M* acetic acid. In the case of tin(IV) the K_D values are reproducible only for higher acetic acid concentrations ($M > 15$). From this molarity a rather sharp decrease of the adsorption function is observed. Below 15 *M* the results are irreproducible, probably because of the tendency of tin(IV) to hydrolyze.

Lead(II) is very strongly adsorbed; it is only possible to give a lower limit for the K_D values ($K_D > 4.9 \cdot 10^4$).

Phosphate, arsenic(III) and (V), antimony(III) and (V) and bismuth(III)

As expected phosphate is eluted directly. Arsenic(III) is eluted directly over the whole range of acetic acid concentration. However, in glacial acetic acid the elution peak showed a long tailing, making total elution difficult. Arsenic(V) was eluted at lower molarities of acetic acid but elution in glacial acetic acid was not possible. Indeed, batch experiments in 15.9 *M* and glacial acetic acid (17.4 *M*) gave K_D values of 1.94 and 69.0, respectively, showing that adsorption in this concentration range is very much influenced by even small amounts of water. Antimony(III) does not give readily reproducible results, probably because of its tendency to hydrolyze. However, the results were computed and are shown by a dotted line in Fig. 6. Antimony(V) is eluted normally in 2.99 *M* acetic acid with only a small tailing effect. In 13.9 *M* acetic acid, the elution peak is not well defined. It is rather flat with a considerable tailing.

Selenium(IV) and tellurium(IV)

Selenium(IV) is quantitatively eluted at all the acetic acid molarities tested. However, the elution peak is not well defined and gives the impression of more than one peak overlapping. This could be caused by more than one valency state of selenium being present in the final solution. Tellurium(IV) behaves very similarly to selenium(IV). It is eluted at all acetic acid molarities. However, elution is not quantitative and a large percentage of the activity is left in the column.

Halogens

As expected, chloride, bromide and iodide do not show any affinity for the resin. They are eluted at all molarities of acetic acid.

SEPARATIONS

In the present study the scope for achieving interesting separations has been very much limited by two factors: first, several of the possible elutions are not quantitative and secondly, most of the elements are very strongly adsorbed. In this situation only the following three separations are possible.

Separation of the mother–daughter pair $^{99}Mo/^{99m}Tc$

The ^{99m}Tc daughter can be eluted from ^{99}Mo–^{99m}Tc mixtures in 1 *M* acetic acid. Molybdenum, which has a K_D value of about 25, remains on the column, while ^{99m}Tc can be collected in the eluate (Fig. 5c; column: h = 5 cm, ∅ = 0.46 cm^2, flow rate: 0.35 ml min^{-1} cm^{-2}).

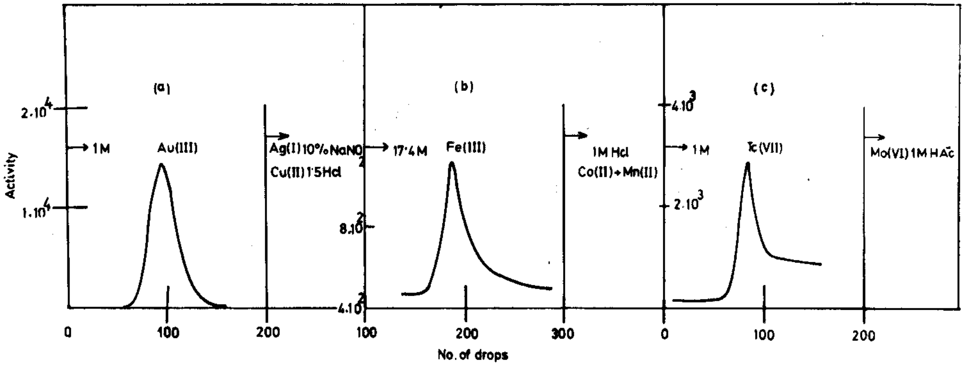

Fig. 5. Separation of (a) Au(III) from Cu(II) and Ag(I), (b) Fe(III) from Co(II) and Mn(II); (c) Tc(VII) from Mo(VI).

Iron from manganese and cobalt

In glacial acetic acid (17.4 *M*), iron(III) flows straight through the column, leaving cobalt(II) and manganese(II) very strongly adsorbed on the column. This provides a method of purification of ^{59}Fe produced by the ^{58}Fe(n,γ) reaction from cobalt impurities and the induced ^{54}Mn activity. Both manganese(II) and cobalt(II) can be removed from the column by dilute hydrochloric acid (Fig. 5b, column: h = 5 cm, ∅ = 0.46 cm^2, flow rate: 0.15 ml min^{-1} cm^{-2}).

Separation of gold from copper and silver

Gold(III) is eluted quantitatively in dilute acetic acid while both copper(II) and silver(I) are held on the column (Fig. 5a, column: h = 5 cm, ∅ = 0.46 cm^2, flow rate: 0.35 ml min^{-1} cm^{-2}). Copper and silver can further be separated as reported by Bhatnagar[14,15].

CONCLUSIONS

The two major effects, resulting from the addition of acetic acid to water, which may affect the adsorbability are:

1. lowering of the dielectric constant ($\varepsilon_{H_2O}=80.3$; $\varepsilon_{HAc}=6.2$), which results in an increase of attraction forces between ions of unlike charge, and therefore favours association or complex formation[5];

2. reduction of the cooperative effect of water dipoles, *i.e.* disruption of hydrogen bonds leading to changes in the ion–water and water–water interactions in both the resin and the external aqueous phase[16].

If the elements are divided in the following four classes, an interpretation of their behaviour in the light of the aforesaid two effects can be attempted.

1. The elements which are so strongly adsorbed over the whole range of acetic acid concentrations that the study of the K_D values as a function of the acetic acid molarity is not possible in the present circumstances. Obviously these elements are present either as their normal cations or as positive complexes.

2. Elements which are adsorbed over the whole molarity range and show significant changes with acetic acid concentration. The K_D values *vs.* acetic acid concentration follow a general trend of being either constant or first decreasing slightly with increasing acetic acid concentration and then after having reached a minimum, increasing rather steeply in the higher acetic acid concentration region.

Besides favouring complex formation with acetate ions, the lowering of the dielectric constant also results in greater attraction of the exchangeable identities (where there are normal cations or positive complexes) with the exchange sites consisting of negatively charged sulphonated groups, thus favouring higher adsorption. The second effect of disruption of hydrogen bonds, by providing more opportunities of ion–water interactions results in an opposite action. The resultant K_D value thus depends on the relative contribution of these two factors. At higher acetic acid concentrations the former appears to predominate. This is further supported by the fact that association between ions of unlike charge increases very rapidly below a certain critical value of dielectric constant which depends on the charges and the radii of ions[5].

A small, highly charged ion will prefer the aqueous phase, as its transfer into the resin requires a loss of hydration energy. However, the larger the ion and the smaller its charge, the smaller its degree of hydration in the aqueous phase and the less hydration energy it can and does lose in passing into the resin phase. Thus, in an exchange process, the larger the ion, the greater the affinity for the resin. The same sequence is followed here by the alkali metals and the alkaline earths:

$\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Rb} < \mathrm{Cs}$ and $(\mathrm{Mg}) < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba}$.

The behaviour of iron(III), indium(III) and tin(IV) probably can be explained on the basis of formation of negatively charged complex $\mathrm{X(Ac)}_n^{-(n-3 \text{ or } 4)}$ n being greater than 3 for iron(III) and indium(III), and 4 for tin(IV).

3. Elements which are directly and quantitatively eluted. Of these elements the halogens are undoubtedly present as their normal anions while others are present as their oxy-anions, or chloro, chloro–aquo, bromide, fluoride or nitrate complexes, depending on the nature of the target compound and the mode of dissolution[17].

4. The fourth and last group consists of elements which are not eluted quanti-

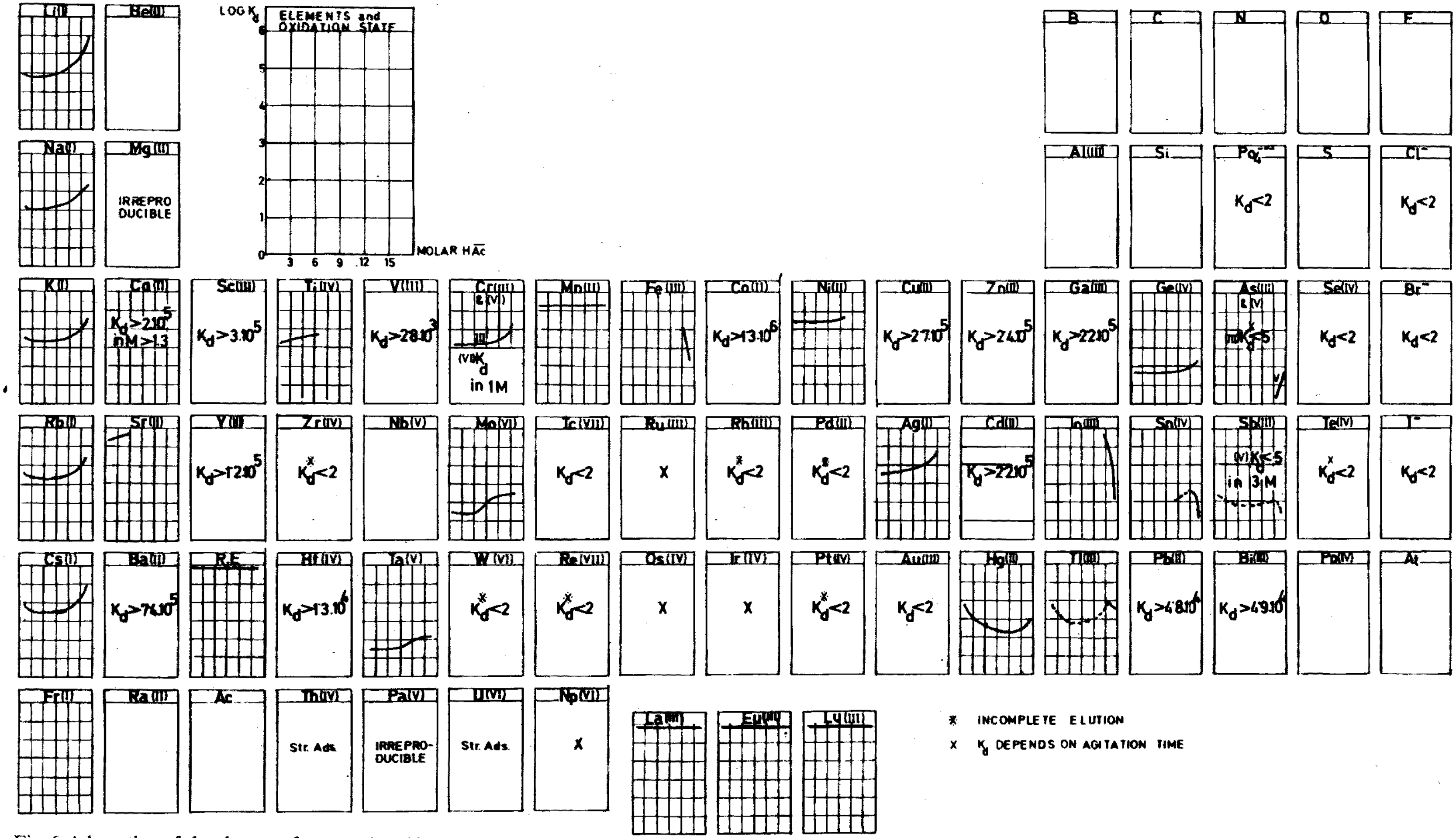

Fig. 6. Adsorption of the elements from acetic acid solutions by a cation-exchange resin.

tatively. Study of K_D values as a function of time in some of these cases indicates that equilibrium is not reached even after 48 h and more. The cation-exchange resins are known to possess significant reducing power. This was made evident by the appearance of precipitates or colour changes in a few cases of the present study.

Thus partial reduction during elution can be regarded as a reason for the elution being not quantitative.

Figure 6 gives a survey of adsorbabilities as a function of acetic acid molarity, for all the elements studied.

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SUMMARY

Adsorbabilities of some 60 elements as a function of acetic acid molarity in the range 1–17.4 *M* have been studied. The separations, technetium from molybdenum, iron from cobalt and manganese, and gold from silver and copper are described. A qualitative interpretation of the adsorbabilities has been attempted.

RÉSUMÉ

Une étude est effectuée sur les adsorbabilités d'environ 60 éléments, en fonction de diverses molarités en acide acétique (1à 17.4 *M*). On décrit les séparations : technétium d'avec molybdène, fer d'avec cobalt et manganèse, or d'avec argent et cuivre.

ZUSAMMENFASSUNG

Die Adsorption von etwa 60 Elementen an einem Kationenaustauscher wurde als Funktion der Essigsäure-Molarität im Bereich 1–17.4 *M* untersucht. Die Trennungen Technetium von Molybdän, Eisen von Kobalt und Mangan sowie Gold von Silber und Kupfer werden beschrieben. Eine qualitative Deutung des Adsorptionsverhaltens wurde versucht.

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DISTILLATION ISOTHERMIQUE DE L'ACIDE BORIQUE SOUS FORME D'ESTER TRIMÉTHYLBORIQUE

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Généralement, le bore est séparé de son milieu sous forme d'acide borique[1-4]. Outre les méthodes de séparation par électrolyse et celle par échangeur d'ions[5] qui permet d'éliminer les cations et anions d'acides forts renfermés dans le milieu à analyser, la distillation de l'ester triméthylborique est la plus couramment utilisée. Bush[6], Luke[7], Spicer et Strickland[8], Philipson[9], Owen[10], Wojtowica et Kubica[11], Masatoshi[12] ont réussi à distiller des masses de bore de l'ordre du μg. A notre connaissance, seuls Umland et Janssen[13] ont étudié la séparation du bore sous forme d'ester triméthylborique en milieu acide sulfurique par distillation isothermique. Leur procédé a ceci de particulier que les réactifs, acide sulfurique et méthanol, entrent au contact l'un de l'autre par l'intermédiaire de la phase vapeur. Cette méthode relativement lente est limitée à la séparation de masse de bore de l'ordre du mg et demande de 6 à 12 h.

Dans le cadre d'une recherche sur le dosage du bore par dilution isotopique en spectrométrie de masse, nous avons mis au point une méthode de distillation isothermique qui doit permettre de séparer quantitativement 50 ng de bore et plus, dans des cuves en polystyrol du commerce. Cette séparation s'avère nécessaire si l'on se trouve en présence de strontium, élément gênant pour la détermination des abondances isotopiques du bore, ou si le bore se trouve en concentration telle dans un solide, que celui-ci perturbe la thermoionisation du borax en $Na_2BO_2^+$. Nous montrerons que la séparation est possible. Les cuves de microdiffusion utilisées dans ce travail renferment du strontium. Nous en avons préparé dans un matériel qui en est exempt et qui sera décrit dans une publication ultérieure.

Principe de la méthode

L'acide borique forme avec les alcools de faible masse moléculaire des esters volatils en milieu acide et déshydratant. L'ester triméthylborique (p.e. 67–68°) est plus favorable que l'ester triéthylborique (p.e. 120°) pour notre séparation.

Les acides pouvant servir de déshydratants et de catalyseurs d'estérification sont l'acide sulfurique et l'acide *p*-toluènesulfonique, solubles dans le méthanol. L'acide sulfurique réagit violemment avec le méthanol, contrairement à l'acide *p*-toluènesulfonique. Ces deux acides forment avec le méthanol des esters à hauts points d'ébullition (292° pour l'ester de l'acide *p*-toluènesulfonique et 188° pour celui de l'acide sulfurique). L'acide sulfurique est préférable, parce qu'il élève rapidement la température du milieu de réaction lorsqu'on le mélange au méthanol.

La distillation isothermique de l'acide borique est l'objet de deux réactions chimiques: la première, celle de l'estérification de l'acide borique se fait dans le compartiment extérieur de la cuve; la seconde, celle de l'hydrolyse de l'ester dans le compartiment intérieur, dépend entre autres de la pression de vapeur de l'ester triméthylborique. Nous avons effectué cette microdiffusion un peu au-dessus du point d'ébullition de l'ester triméthylborique pour en augmenter la vitesse.

ÉTUDE DE LA MICRODIFFUSION

Les facteurs affectant le rendement de microdiffusion sont: le volume de méthanol par rapport à celui de solution sulfurique, la surface et la composition de l'absorbant, et la cinétique de microdiffusion. Le bore, après séparation, a été dosé par la méthode fluorimétrique à l'HMCB selon Marcantonatos *et al.*[14-16].

Appareillage

Les cuves utilisées sont des cuves Falcon No. 7004 (Dickinson et Co). Elles conviennent fort bien au dosage fluorimétrique du bore après la séparation. Elles sont très "mouillantes", si bien qu'il faut travailler avec des volumes inférieurs à 0.5 ml, pour éviter un mélange des réactifs avant leur fermeture. Ce faible volume nous a cependant permis d'étudier une cinétique de microdiffusion.

Les mesures de fluorescence ont été effectuées au moyen d'un fluorimètre Eppendorf équipé d'un multiplicateur de photons et d'une lampe à mercure. La sélection des longueurs d'onde se fait à l'aide de deux filtres, le premier de 366 nm pour l'excitation, le second de 450 à 3000 nm pour la fluorescence. L'appareil est calibré par l'étalon fluorescent Zeiss No. 5554.

Influence du volume de méthanol

Des volumes croissants de méthanol sont ajoutés dans des cuves renfermant 100 ng de bore dans 0.1 ml d'acide sulfurique dans le compartiment extérieur et 0.5 ml d'une solution NaOH à 2 μg ml^{-1} dans le compartiment intérieur. Une série de

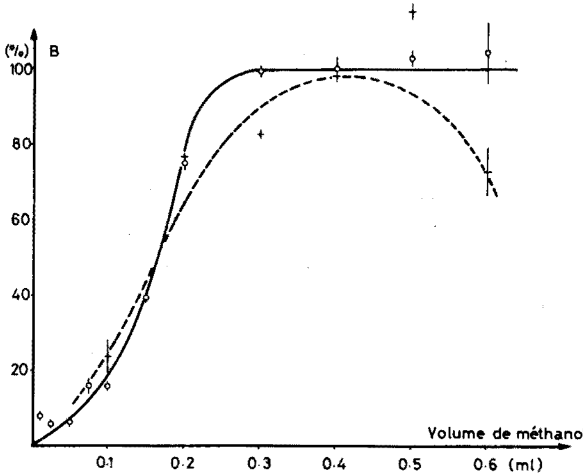

Fig. 1. Rendement du bore distillé. B(%) = f(volume de méthanol). 100 ng de bore dans 0.1 ml H_2SO_4, 0.5 ml de NaOH à 2 μg ml^{-1}, 30 min de microdiffusion à 70°. (○) Sans agitation. (+) Avec agitation.

mesures identiques a été faite mais en agitant les cuves à 50 cycles s^{-1} avec une amplitude de 0.5 mm.

Nous donnons à la Fig. 1 le rendement du bore distillé en % (B %) en fonction du volume de méthanol et les écarts standard sur la moyenne. On constate qu'il faut au moins 0.3 ml de méthanol pour une distillation quantitative de 100 ng de bore (B % ≥99 %). Lorsque la cuve est mise en vibration, on assiste à une forte diminution du rendement, si le volume de méthanol est supérieur à 0.4 ml. Cela est dû à une diminution de la surface de l'absorbant: l'eau de la solution de soude est évaporée rapidement à cause de l'agitation, puis absorbée par l'acide sulfurique. De plus, comme le montre la Fig. 4, le sulfate de diméthyle "microdiffuse" aussi et neutralise rapidement l'absorbant. L'agitation n'augmente en fait que la vitesse d'évaporation de l'eau et celle du sulfate de diméthyle. La vitesse de microdiffusion du bore est telle que l'agitation ne présente aucun intérêt.

Influence du volume d'absorbant renfermant 2 $\mu g\ ml^{-1}$ de NaOH

Trois séries d'expériences permettent de se faire une idée du rôle du volume de l'absorbant et de sa concentration en soude. La Fig. 2 donne le rendement de séparation

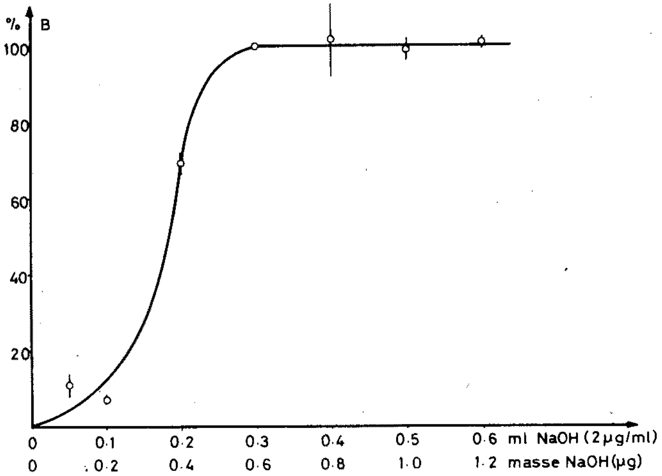

Fig. 2. Rendement de la séparation de 100 ng de bore par microdiffusion en fonction de la masse de soude

NaOH (ml)	*No.*[a]	*B (%)*	s_r[b]
0.05	3	11.1	3.1
0.10	4	7.2	1.3
0.20	3	69.5	2.3
0.30	3	100.6	0.6
0.40	3	102.0	9.1
0.50	3	99.5	2.8
0.60	3	101.0	1.4

[a] Nombre de mesures.

[b] Ecart standard sur la moyenne.

de 100 ng de bore en solution dans 0.1 ml d'acide sulfurique et réagissant avec 0.3 ml de méthanol en fonction du volume variable de solution de soude à 2 μg ml^{-1} servant d'absorbant. Le volume de 0.3 ml de méthanol a été choisi parce qu'il permet de manipuler aisément les cuves de Conway et parce que la vitesse de microdiffusion est inversément proportionnelle au volume de solution à séparer. La masse minimum d'hydroxyde de sodium permettant une séparation quantitative est de 0.6 μg, soit 0.3 ml, volume utilisé par la suite.

Influence du volume d'eau du compartiment intérieur (masse de NaOH constante = 0.8 μg)

La Figure 3 donne le rendement de microdiffusion en fonction du volume de l'absorbant renfermant une masse constante de NaOH 0.8 μg. Deux essais effectués avec une pastille de soude solide comme absorbant montrent que le rendement de microdiffusion est quasi nul. Ceci peut provenir de la faible surface de la pastille qui peut être recouverte par une couche de sulfate de diméthyle et d'ester triméthylborique. Une pastille de soude broyée donne un résultat aberrant dû aux contaminations provoquées par le broyage. Ces résultats n'ont pas été reportés dans la Fig. 3.

Un volume de 0.3 ml de solution de soude recouvre entièrement le compartiment intérieur d'une cuve Falcon (environ 8.9 cm^2) sur une épaisseur d'environ 0.25 mm. Pour des volumes plus petits, une partie du compartiment central n'est pas mouillée et le rendement diminue: on peut supposer que le phénomène le plus lent

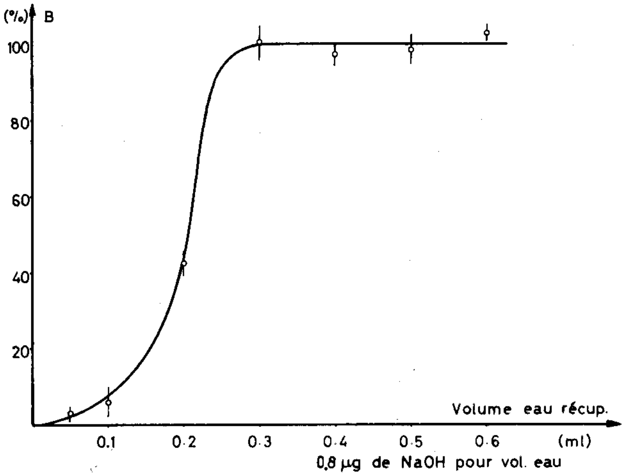

Fig. 3. Influence du volume d'eau servant d'absorbant sur le rendement de microdiffusion B (%) pour 100 ng de bore. 30 min de microdiffusion à 70°.

Eau (ml)	*No.*	*B (%)*	s_r
0.05	3	3.3	2.0
0.1	3	5.6	4.3
0.2	3	42.6	3.4
0.3	6	101.0	4.5
0.4	3	97.7	3.1
0.5	3	98.2	3.7
0.6	3	103.0	1.4

est l'absorption de l'ester triméthylborique. Il est lié directement à la surface d'absorption. Dès que l'on se trouve en présence de 0.3 ml ou plus, la surface de récupération reste à peu près constante pendant les 30 premières minutes de microdiffusion. Le rendement est voisin de 100 %. Dans ces conditions-là, l'étude de la cinétique de la réaction peut être entreprise. Une expression mathématique de ce phénomène, dans laquelle intervient la surface de l'absorbant, n'est pas facile à établir, car celle ci n'a pu être mesurée pour de faibles volumes.

Remarque. Une série de mesures effectuées en utilisant 0.3 ml de solution de méthanol renfermant de 0.25 à 2.0 μg de NaOH, montre que le rendement de microdiffusion ne dépasse jamais 2 %, valeur qui peut être considérée comme erreur statistique. Ce phénomène met en évidence le rôle indispensable de l'eau.

HMCB–H_2SO_4—complexant du bore comme absorbant

Il aurait été intéressant de pouvoir absorber le bore dans un milieu qui le complexe, notamment celui dans lequel on le dose : 0.4 ml de HMCB (à 52.5 μg ml^{-1}) en milieu sulfurique. Les mesures sont effectuées en cuve Falcon où sont placés 0.1 ml de solution sulfurique de bore et 0.3 ml de méthanol. Après 30 et 60 min de microdiffusion à 70°, on récupère le contenu du compartiment central que l'on rince trois fois par un volume total de 2 ml d'acide sulfurique. On complète le volume à 3.0 ml avec H_2SO_4 conc. et on développe la fluorescence. Les résultats sont reportés dans le Tableau I. Le rendement de microdiffusion est dans ces conditions peu élevé.

Les blancs des mesures Falcon étant plus élevés que ne l'indique la méthode, nous avons utilisé des cuves en téflon de forme semblable aux cuves Falcon. Nous obtenons des rendements de microdiffusion voisins. La séparation est moins quantitative après 60 min de réaction qu'après 30 min.

TABLEAU I

MICRODIFFUSION DE 16.6 ET 50 ng DE BORE AVEC UNE SOLUTION SULFURIQUE DE HMCB COMME ABSORBANT

(B_0 = masse de bore à séparer, No. = nombre de mesures. Les cuves en téflon sont de forme semblable aux cuves Falcon)

Temps microdiff. (min)	B_0 *(ng)*	*No.*	*B (%)*	s_r	*Cuve*
30	16.6	4	18	4	Falcon
30	50	3	19	2	Téflon
60	16.6	3	4	3	Falcon

Cinétique de microdiffusion

Elle dépend de la vitesse de formation de l'ester triméthylborique, de la vitesse de diffusion de celui-ci, de la vitesse de vaporisation qui, à 70°, doit être grande, et de la vitesse d'absorption dans le compartiment central. Dans les conditions expérimentales, les 0.4 ml de solution qui recouvrent le compartiment extérieur ont une épaisseur voisine de 0.25 mm, si bien que l'on peut négliger la vitesse de diffusion de l'ester et écrire la loi de microdiffusion sans tenir compte du volume de solution à séparer :

$$B = B_0\,(1-10^{-kt}),$$

où B_0 est la masse initiale de bore, B la masse de bore distillée au temps t, et k la constante de microdiffusion (min^{-1}).

Dans les conditions définies précédemment, c'est-à-dire 0.3 ml de solution renfermant 0.8 μg de NaOH, 0.1 ml de solution sulfurique renfermant 100 ng de bore et 0.3 ml de méthanol, nous avons établi la courbe du rendement de la microdiffusion en fonction du temps (Fig. 4). Elle n'obéit à la loi cinétique qu'au cours des 40 premières minutes. Il faut à peu près deux minutes pour que les 50% du bore distillent. A ce moment, la constante de microdiffusion est évaluée à 0.15 min^{-1}. Pour des temps de microdiffusion de 5 à 10 min, k est voisin de 0.23 min^{-1}. Ces différences proviennent de l'imprécision sur le temps initial qui est celui où le mélange des deux solutions du compartiment extérieur semble homogène. La cinétique est si rapide qu'il est inutile d'agiter les cuves au cours de la réaction.

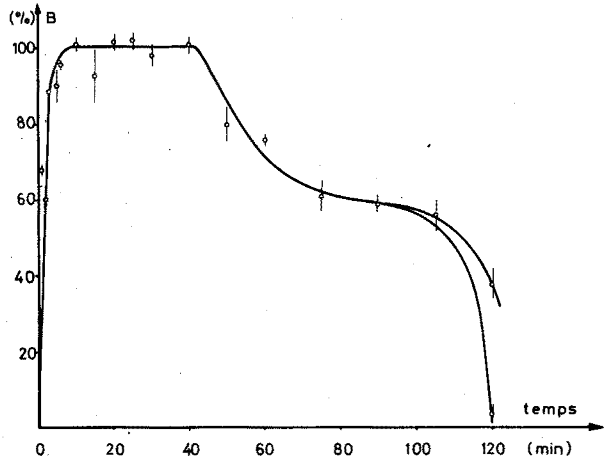

Fig. 4. Cinétique de microdiffusion. Température de microdiffusion, 70°. Masse de bore à séparer, 100 ng.

La deuxième partie de la courbe de la Fig. 4 montre qu'après 10 min les 100 ng de bore ont distillé. Cette quantitativité se maintient pendant 40 min, puis le rendement diminue. Pour expliquer ce phénomène, nous avons suivi la variation du pH du compartiment intérieur au cours de la distillation (Fig. 5). On procède comme ci-dessus, mais en présence de concentrations de NaOH de 26.6 $\mu\text{g ml}^{-1}$ et 2.0 $\mu\text{g ml}^{-1}$ pour montrer le peu d'influence qu'elles ont sur l'allure de la courbe.

La courbe de la Fig. 5 comprend trois zones. La première montre une chute quasi instantanée du pH qui se maintient aux environs de 1 durant les 30 à 40 premières minutes dans la deuxième, puis descend dans la troisième jusqu'à 0. Il n'a pas été possible de mesurer des pH pour des temps supérieurs à 120 min, le volume de l'absorbant ayant par trop diminué. Il n'y a pas de passage mécanique de la solution du compartiment extérieur jusqu'au centre de la cuve. En mettant du méthyle orange dans l'acide sulfurique, on ne constate aucune coloration dans le compartiment central, même au bout de deux heures de microdiffusion.

La cinétique de microdiffusion peut s'expliquer ainsi : les 40 premières minutes

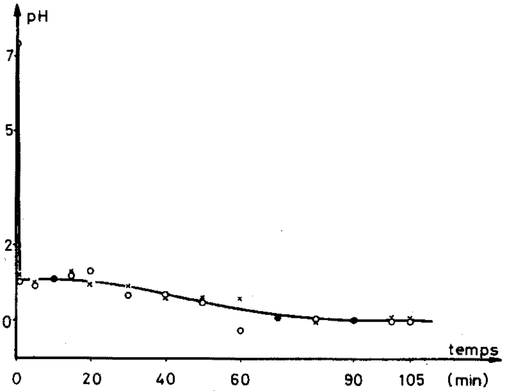

Fig. 5. Variation du pH en fonction du temps dans le compartiment intérieur d'une cuve de microdiffusion. (○) NaOH 26.6 $\mu g\ ml^{-1}$, (×) NaOH 2 $\mu g\ ml^{-1}$.

de microdiffusion n'appellent aucun commentaire: le rendement est maximum, le pH du compartiment intérieur est voisin de 1. Après ce temps, le rendement baisse jusqu'à 60 %. Parallèlement, le pH diminue aussi. Le diméthyle sulfate est hydrolysé par l'eau du compartiment intérieur. Pendant ce temps, l'acide sulfurique du compartiment extérieur agit comme déshydratant et assèche progressivement le compartiment intérieur. On arrive à un équilibre. Le milieu de la cuve est suffisamment acide pour pouvoir à son tour estérifier du triméthylborate et le volatiliser. Il n'est pas étonnant de trouver ainsi un palier pour un rendement qui correspond assez grossièrement au rapport des surfaces du compartiment intérieur et du compartiment extérieur.

Dans la dernière partie de la courbe, au delà de 100 min, l'eau est absorbée plus ou moins complètement par l'acide sulfurique: deux catégories de rendement nettement distinctes apparaissent; le rendement descend jusqu'à 38 % s'il reste des traces d'eau et tombe au voisinage de zéro si le compartiment central est sec. L'eau est donc nécessaire à l'absorption de l'ester triméthylborique.

MODE OPÉRATOIRE

On met dans les cuves de microdiffusion dont les bords ont été préalablement graissés, dans l'ordre:

- 0.3 ml d'une solution de NaOH à 2 $\mu g\ ml^{-1}$ dans le compartiment central
- 0.10 ml d'acide sulfurique (p.a. Merck) pour le blanc ou 0.10 ml de solution à analyser dans le compartiment extérieur, près de la paroi mitoyenne
- 0.3 ml de méthanol (p.a. Merck) de l'autre côté de la paroi mitoyenne du compartiment extérieur.

Immédiatement après l'adjonction de ce dernier, on ferme hermétiquement la cuve. Les volumes entrant en réaction sont assez faibles pour qu'il ne soit pas nécessaire de fixer le couvercle à l'aide de pinces, si la cuve n'est pas mise en vibration. La graisse mise sur les bords en assure l'étanchéité.

On laisse les cuves durant 30 min à l'étuve à 70°. On transvase le contenu de l'enceinte intérieure dans un ballon jaugé de 10 ml. On lave trois fois avec 2 ml d'acide sulfurique. Les fractions sont introduites dans le ballon jaugé. On procède ensuite au dosage du bore par l'HMCB.

Détermination de la limite de sensibilité

La formule cinétique ne fait pas intervenir la masse de bore en ce qui concerne le rendement, ni la vitesse de microdiffusion. Aussi, s'agit-il de déterminer la masse de bore pouvant être encore séparée quantitativement. Dans les conditions définies à la Fig. 6, on peut distiller au maximum 100 ng de bore, même si le mélange en contient davantage: c'est ainsi qu'environ 43 % de bore sont séparés pour 200 ng, 88 % pour 150 ng et 100 % pour 100 ng. Pour les masses inférieures à 50 ng (trait pointillé), l'imprécision de la méthode due aux manipulations l'emporte sur tout autre phénomène. On peut donc séparer quantitativement et avec une précision suffisante 50 à 100 ng de bore en solution dans 0.1 ml d'acide sulfurique qui réagissent avec 0.3 ml de méthanol; 0.3 ml d'eau pouvant renfermer 8 μg de NaOH ou plus suffisent à l'absorption de l'ester triméthylborique.

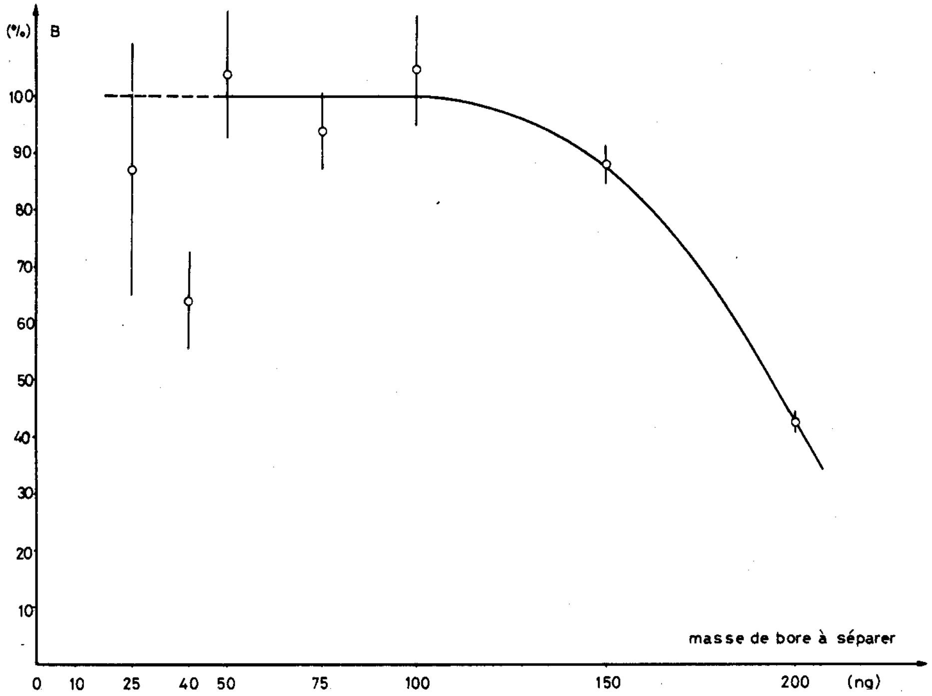

Fig. 6. Détermination de la limite de sensibilité de la séparation du bore par distillation isothermique dans des cuves "Falcon".

Bore (ng)	*No.*	*B (ng)*	*B (%)*	s_r
200	3	85.9	42.9	1.7
150	3	132.1	88.0	3.1
100	2	105.4	105.4	
75	3	70.5	94.0	6.8
50	2	51.9	103.8	11.4
40	3	25.6	64.0	8.5
25	3	21.8	87.1	22.4

CONCLUSION

L'expérience montre que la microdiffusion du bore est possible et que la mesure de la masse de bore séparée peut se faire par fluorimétrie ou colorimétrie. Par contre, les mesures du rendement par spectrométrie de masse s'avèrent impossibles à cause de la présence de strontium. Le pic de $^{88}Sr^+$ est en effet si intense qu'il est impossible de déterminer les abondances isotopiques du bore sous forme d'ion $^{88}Na_2BO_2^+$ et $^{89}Na_2BO_2^+$. Les cuves de microdiffusion devront dans ce cas être exemptes de strontium.

RÉSUMÉ

La séparation quantitative par distillation isothermique de 50–100 ng de bore en solution dans 0.1 ml d'acide sulfurique et concentré est possible en 10 min si l'on fait réagir la solution sulfurique avec au moins 0.3 ml de méthanol et que l'on absorbe l'ester triméthylborique par 0.3 ml de solution de NaOH à 2 μg ml^{-1}. Les mesures du rendement de séparation se font par fluorimétrie à l'HMCB.

SUMMARY

The quantitative separation by isothermal distillation of 50–100 ng of boron in 0.1 ml of sulfuric acid solution is possible in 10 min, if the sulfuric acid solution is made to react with 0.3 ml of methanol, and the trimethylboric ester formed is absorbed by 0.3 ml of sodium hydroxide solution at a concentration of 2 μg ml^{-1}. Boron in the distilled fractions is measured by a fluorimetric method with HMCB.

ZUSAMMENFASSUNG

Die quantitative Abtrennung von 50–100 ng Bor in 0.1 ml Schwefelsäurelösung durch isotherme Destillation ist in 10 min möglich, wenn die Schwefelsäurelösung mit 0.3 ml Methanol umgesetzt wird und der gebildete Borsäuretrimethylester durch 0.3 ml Natronlauge bei einer Konzentration von 2 μg ml^{-1} absorbiert wird. Die Bestimmung von Bor in den destillierten Fraktionen erfolgt fluorimetrisch unter Verwendung von HMCB.

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SHORT COMMUNICATION

Mass spectrometry of DOPA and analogues

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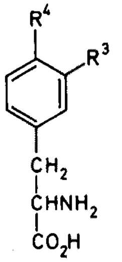
Amino acids are normally esterified, acylated, reduced or otherwise chemically modified before analysis by mass spectrometry[1]. The free amino acids, because of their zwitterionic character, have a very low vapour pressure. Sufficient vapour pressure of the more stable amino acids, however, can be attained by use of the direct insertion technique[2,3]. Mass spectrometric quantitative analysis of aliphatic amino acid mixtures by direct insertion into the ionization chamber has been claimed, but the method failed when the mixture also contained the much less volatile aromatic amino acids[4]. On the other hand, free or acylated aromatic amino acids have been reported to have a very dominant base peak in their spectra, owing to β-cleavage to the aromatic ring[2,5]. This indicated that mass spectrometry by the direct insertion technique might be a rapid and sensitive means of analysis of phenylalanine analogues. Of great interest in this connection is the estimation of 3,4-dihydroxyphenylalanine (DOPA), which is widely used in the treatment of Parkinsonism. Most methods presently in use for DOPA analysis in biological tissues involve chromatographic isolation and fluorimetric determination[6]. Because of the small amounts of material available from biological tissues, such methods would hardly detect minor metabolic components formed from DOPA and present in the DOPA isolate. Since a characteristic and intense fragment varies systematically with the nature of the aromatic amino acid, any metabolic or chemical change of the benzyl moiety in DOPA should become apparent from the spectrum of the DOPA sample.

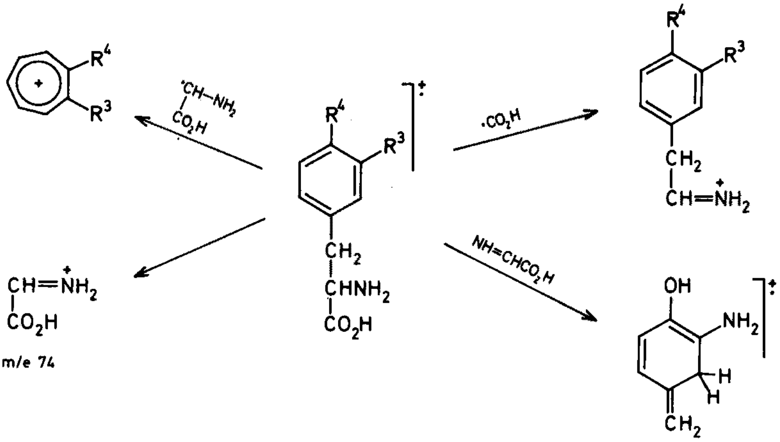
Phenylalanine can be regarded as the parent compound in the series I–VI investigated.



I $R^3 = R^4 = H$
II $R^3 = H, R^4 = OH$
III $R^3 = R^4 = OH$
IV $R^3 = OCH_3, R^4 = OH$
V $R^3 = OH, R^4 = OCH_3$
VI $R^3 = NH_2, R^4 = OH$

The main features in the mass spectra of phenylalanine and tyrosine have already been reported[2,3]. Deviations in relative peak intensities occur, however, because of inherent instrumental differences and experimental conditions. These spectra have therefore been included in Table I. It is seen that all compounds give weak molecular ions. With the exception of phenylalanine, most of the ion current is carried by the [M-74] species formed by β-cleavage $[\mathrm{R^3,R^4C_6H_3\overset{+}{C}H_2}]$ to the aromatic nucleus. In phenylalanine charge retention is favoured on the nitrogen to the extent that the *m/e* 74 species $[\mathrm{\overset{+}{N}H_2{=}CH{-}CO_2H}]$ give rise to the base peak. Retention of the charge on the benzyl moiety only accounts for 60% relative peak intensity. In the substituted phenylalanines (II–VI) the peak intensity of the *m/e* 74 species is only of the order 2–6%. As in simple amino acids, the $[\mathrm{M{-}CO_2H}]$ ions are important in the spectra of phenylalanine (50%) but only amount to 1–2% for the substituted analogues. The marked difference in the spectra of phenylalanine and its analogues must lie in resonance stabilization of the ion formed on ring β-cleavage, for all the analogues carry electron-donating substituents in the *para* position. That the direction of fragmentation is governed by the stabilization of the ion formed is also evident from the literature. Thus in the spectra of the three isomeric anisoles, the [M-1] peak is most pronounced in the spectrum of the *p*-isomer[7]. Predominant benzyl cleavage has also been observed in *p*-alkylphenols but not in the *m*-isomer because resonance stabilization is excluded[8].

In the 3-amino isomer (VI), β-cleavage with transfer of one hydrogen into the aromatic nucleus, has some importance (*m/e* 123). The signal at this mass unit also contains the isotope ion from *m/e* 122.



From Table I it is seen that the 3-methoxy (IV) and the 4-methoxy (V) isomers have very similar spectra. The small differences in relative abundance are not sufficient for identification. With the reasonable assumption that the sensitivity of this closely related class of compounds is approximately the same, quantitative mixture analysis should be possible except for such isomeric pairs as IV and V.

The 3-methoxy isomer (IV) is a metabolic product formed in low amounts from DOPA circulating in the blood in patients receiving treatment[6]. Simple O-alkylated DOPA derivatives are also expected impurities in DOPA prepared synthetically from the corresponding benzaldehyde[9]. For this reason a determination of IV in DOPA was attempted. In an effort to prepare homogeneous mixtures, separate methanolic

TABLE I

RELATIVE INTENSITIES OF THE MAJOR IONS IN THE MASS SPECTRA OF PHENYLALANINE ANALOGUES BY THE DIRECT INSERTION TECHNIQUE

I		*II*		*III*		*IV*		*V*		*VI*	
m/e	*%I*	*m/e*	*%I*	*m/e*	*%I*	*m/e*	*%I*	*m/e*	*%I*	*m/e*	*%I*
165	1.0	181	2.3	197	3.6	211	3.3	211	4.3	196	10.7
121	4.4	136	3.0	152	2.5	166	1.8	166	2.1	151	1.7
120	49.5	135	1.3	151	1.2	138	10.3	138	11.3	134	2.2
119	2.8	108	12.1	124	12.7	137	*100*	137	*100*	124	1.6
118	3.2	107	*100*	123	*100*	123	2.8	123	3.6	123	19.6
117	1.7	91	4.5	107	2.6	122	8.3	122	8.3	122	*100*
104	3.1	77	7.3	105	1.9	94	4.5	94	4.8	121	2.1
103	10.1	74	4.4	78	2.0	77	3.3	77	2.9	106	3.3
93	3.2	68	2.2	77	9.8	74	2.2	74	2.2	94	5.2
92	17.1	53	2.3	76	2.2	51	2.9	51	2.3	93	1.9
91	58.9	51	2.2	75	2.8					80	2.0
77	9.8	44	2.2	74	5.8					78	2.0
75	3.4			53	4.3					77	6.3
74	*100*			51	6.2					74	2.0
65	15.1			44	4.8					67	2.5
63	4.9									53	2.2
51	8.3									51	4.0
46	9.8									44	3.2

solutions of the components were mixed quantitatively and introduced into the instrument by the direct insertion technique. By this method it was found that in a 3-μg sample of DOPA the lowest detection limit for the 3-methoxy analogue (IV) was 30 ng (1 % relative concentration). Larger samples of the order of 200 μg were used to investigate the quantitative relationship between peak intensity and component concentration, by applying the method of Hites in quantitative analysis of triglycerides[10]. At very low concentrations of the 3-methoxy isomer (IV), however, the results were not easily reproducible. A major reason for this is inherent in the method itself. The technique involves free sublimation from the surface of a solid mixture in the source region, and the relative gas phase concentration will depend on the homogeneity of the exposed surface of the solid mixture; but surface homogeneity becomes difficult to achieve at low relative concentration. Another important factor is the difference in relative vapour pressure of the components, *e.g.* the 3-methoxy isomer is more volatile than DOPA. With time, the relative surface concentration will change and thereby the relative gas phase concentration will change. Except for the above quantitative limitations to very low relative concentrations, however, mass spectrometry should prove useful for detection and semiquantitative estimation of DOPA-like substances.

Experimental

The compounds were analyzed on an AEI MS 902 mass spectrometer attached to an AEI DS 30 data system. The ionizing energy was 70 eV and the source temperature 240°. The heated direct insertion probe was used. The samples were placed in a 18-

mm long melting-point tube at the end of the probe. The gain was set at maximum during all experiments. To establish the minimum detectable amounts of substance the methanolic solution was transferred to the melting-point tube and the solvent removed in a stream of hot air. The best evaporation temperature was 180° with a trap current of 500 μA. Three spectra were recorded within 2 min when the sample was completely evaporated. With the larger samples (200 μg) the solid was transferred directly to the melting-point tube.

Spectra were recorded at constant temperature and constant ion current (several minutes). Before the evaporation temperature was chosen, the temperature had been varied from 150 to 250°.

The samples used in this work were made available to us by Weiders Farmasøytiske, Oslo.

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SHORT COMMUNICATION

Neutron activation analysis of high-purity selenium

Part VI. Determination of antimony

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In previous publications[1], procedures have been described for the neutron activation analysis of high-purity selenium. None of these methods was suitable for determining antimony, since this element was not separated from the matrix activities ^{75}Se, ^{77}As, ^{76}As, ^{74}As. A special approach was therefore required. The analytical problem consists of separating ^{122}Sb from the intense ^{75}Se activity, and from the arsenic activities, even when counting with a Ge(Li) detector, because of the low antimony concentrations involved. It is better to base the determination on ^{122}Sb, rather than ^{124}Sb, in order to keep the induced ^{75}Se matrix activity reasonably low.

Relevant nuclear data are shown in Table I.

Röhnsch[4] described a procedure for the simultaneous determination of several elements, including antimony, in high-purity selenium. After the irradiated sample had been dissolved in nitric acid, in the presence of carriers, the solution was evaporated, the residue was taken up in 4 *M* hydrochloric acid, and selenium was precipitated with hydrazine sulfate. Residual ^{75}Se activities were reduced by reprecipitations after addition of selenium carrier. After extraction of arsenic from the filtrate, antimony(V) was extracted with isopropylether (together with Tl and Fe) and further purified by extraction and precipitation. Counting was carried out with a G.M. counter or a scintillation counter.

Neutron activation analyses for antimony in selenium are also described by Yakovlev *et al.*[5], by a similar separation method, and by Mathieu[6] and Gobrecht *et al.*[7]. The latter authors took advantage of the large resonance integral cross-section of ^{121}Sb to increase the ^{122}Sb/^{75}Se activity ratio by irradiating under a cadmium cover. It is obvious that this procedure decreases the ^{122}Sb/^{74,76,77}As ratio. Typical antimony concentrations, reported in high-purity selenium are: 10 p.p.b.[6]; < 16 p.p.b.[4]; 20; 4 and < 1 p.p.b.[7]. Yakovlev *et al.*[5] report 16–60 p.p.m.

In the present investigation the selenium activity was removed by reductions with hydroxyammonium chloride and the arsenic activity by distillation, after which antimony was precipitated as the sulfide, and counted with a Ge(Li) detector. High-resolution γ-spectrometry was necessary in order to discriminate against photopeaks from the natural background and from ^{76}As and ^{74}As activities. The chemical yield was determined by titration with bromate, after dissolution of the sulfide in sulfuric acid.

TABLE I

RELEVANT NUCLEAR DATA[a]

Reaction	*Isotopic abundance* (%)	*Cross-section* σ_0	$T_{\frac{1}{2}}$ *formed*	*Decay mode*	*γ-Energies* (*absolute intensities %*)
$^{121}Sb(n, \gamma)^{122}Sb$	57.25	6.2 b	67.2 h	β^+, β^-, EC	564.0(66.3); 692.5(3.3); 1140.5(0.7); 1256.6(0.7)
$^{123}Sb(n, \gamma)^{124}Sb$	42.8	3.45 b	60.3 d	β^-	602.7(98); 722.7(9.8); 1691.0(50); others
$^{74}Se(n, \gamma)^{75}Se$	0.87	30 b	120.4 d	EC	66.0(1); 96.7(3.5); 121.1(17.6); 136.0(60.5); 198.6(1.5); 264.6 (63.0); 279.5(26.5); 303.9(1.4); 400.6(12.6); 427.0 (< 0.1); 572.0(0.1); 628.0(< 0.1)
$^{74}Se(n, p)^{74}As$	0.87	16 mb[b]	17.9 d	β^+, β^-, EC	595.9(55); 608.4(0.1); 634.7 (14.1); 1204.0(0.3); others (< 0.1)
$^{76}Se(n, p)^{76}As$	9.02	0.17 mb[b]	26.5 h	β^-	559.1(44.0); 562.8(0.4); 657.0 (6.6); 1216.2(4.4); 1220.0 (0.9); 1228.6(1.0); 2096.6(0.6); others (< 0.4)
$^{77}Se(n, p)^{77}As$	7.58	0.38 mb[b]	38.8 h	β^-	87.9(0.4); 161.9(0.5); 239.0(2.5); 270.7(< 0.1); 281.6(0.1); 520.6 (0.9)

[a] Data mainly from Pagden *et al.*[2].

[b] Average cross-section in a fission neutron spectrum, from Deschuyter and Hoste[3].

Reagents

Antimony carrier. Dissolve 1.5 g of antimony in 13 ml of 12 *M* hydrochloric acid and 4 ml of 14 *M* nitric acid while heating. Transfer the solution to a 250-ml volumetric flask, add 80 ml of 12 *M* hydrochloric acid, and dilute to the mark with water. This stock solution contains *ca.* 6.3 mg Sb ml^{-1} in *ca.* 4 *M* hydrochloric acid.

Selenium carrier. Transfer 1 g of selenium to a 250-ml flask equipped with a reflux condenser, and dissolve in 15 ml of warm concentrated nitric acid. Expel nitrogen oxides by further heating while adding 65 ml of 12 *M* hydrochloric acid during 1 h. Dilute to 100 ml with water. This solution contains *ca.* 10 mg Se ml^{-1} in 7 *M* hydrochloric acid.

Irradiation

Seal the 1-g selenium samples (grains) in clean quartz tubes. Prepare standards (1–2 mg of "soluble" Sb_2O_3) in the same way, after sealing the sample ampoules to avoid any contamination. The irradiations were carried out for 3 h in the Thetis reactor of the Institute ($\phi_{th} = 7 \cdot 10^{11}$ n cm^{-2} s^{-1}; $\phi_{th}/\phi_{epi} = 43$; $\phi_{th}/\phi_f = 17.5$).

Procedure

One day after irradiation, etch the selenium sample three times with 4 *M* nitric acid, rinse with water and transfer to a 1-l flask equipped with a 30-cm reflux condenser. Dissolve the sample in 15 ml of concentrated nitric acid after adding 20 ml of Sb carrier solution. Then add hydrochloric acid under continued heating to free the solution from nitrogen oxides (70 ml of 12 *M* HCl, 4–5 h heating). Add 50 ml of water, 15 g of hydroxyammonium chloride, and 75 ml of 6 *M* hydrochloric acid and heat at *ca.* 80° for several hours. Selenium is precipitated as the red, monoclinic modification, which is later transformed to the black, hexagonal allotropic form. Filter off the precipitate, wash with water and 6 *M* hydrochloric acid, and discard. Transfer the filtrate again to the 1-l flask, add *ca.* 7 ml of Se carrier solution (70 mg Se) and 5–10 g of hydroxyammonium chloride, and heat at *ca.* 80° for a few hours. Inspect the filtrate of the second reduction by γ-ray spectrometry. (The filtrate usually appeared to be almost free of ^{75}Se, although a third precipitation was sometimes required.)

Transfer the filtrate, which contains mainly ^{77}As, ^{76}As and ^{74}As activities and residual ^{75}Se, to a distillation flask and boil for 3 h while adding 50 ml of 12 *M* hydrochloric acid (temp. 105–120°). Discard the distillates.

In the residue, precipitate the antimony with thioacetamide from a homogeneous 1 *M* hydrochloric acid solution as its sulfide. Collect the precipitate in a filter crucible and wash with 1 *M* hydrochloric acid +0.01% thioacetamide. Carry out the Ge(Li) γ-spectrometry on a 40-cm^3 detector with a resolution of 2.4 keV for ^{60}Co and an efficiency of 5%, compared to a 7.5 × 7.5 cm NaI(Tl) for the same isotope, during at least 15 h.

Dissolve the standards (1–2 mg Sb_2O_3) in a few ml of concentrated nitric acid and dilute with 1 *M* hydrochloric acid. Precipitate antimony as its sulfide, and measure in the same way as the unknown samples.

For the chemical yield determination, dissolve the sulfide in 7 ml of concentrated sulfuric acid. After carefully adding 170 ml of water, 50 ml of 12 *M* hydrochloric acid and 1 g of sodium sulfite, remove excess of sulfur dioxide by boiling for 10 min, and aerating for 3 min. While still hot ($>70°$) titrate antimony(III) with 0.1 *N* potassium bromate, using methyl orange indicator (blank less than 0.4 ml of 0.1 *N* titrant).

For the standards, the chemical yield was 100%; for the samples it varied from 85 to 96%.

Results and discussion

It appears that two to three reduction steps reduced the ^{75}Se activity to *ca.* 10^{-4}%. This means that, under the described experimental conditions, the most intense ^{75}Se peaks (96.7, 121.1, 136.0, 264.6, 279.5 keV) can still be observed in the final antimony fraction. The 400.6-keV line (absolute intensity 12.6%) is just above background level, whereas the 572.0-keV line (absolute intensity 0.1%) could never be detected. The decontamination factor is thus sufficient for the present purpose.

The distillation step removes typically more than 95% of the arsenic activity. This is sufficient for the determination of antimony at the p.p.b. level with a Ge(Li) detector. Redistillation and/or irradiation in a better thermalized neutron spectrum would, of course, further reduce the arsenic contamination.

Figure 1a shows the γ-ray spectrum (500–625 keV) of an antimony sulfide precipitate from an irradiated selenium sample, 7 days after activation. The 564.0-keV peak of ^{122}Sb is used for the determination. Figure 1b proves that the natural background is essentially flat in this energy region. The arsenic contamination can be seen, mainly 17.9-d ^{74}As (595.9 and 511.0 keV), but also 26.5-h ^{76}As (559.1 keV) and

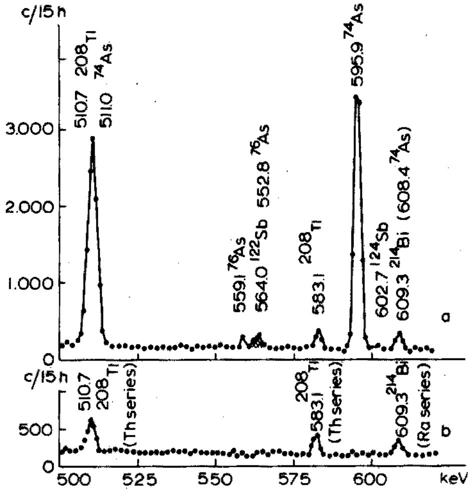

Fig. 1. γ-Ray spectra recorded with a 40-cm^3 Ge(Li) detector. (a) Sb precipitate separated from Se sample 2; (b) background spectrum.

even some ^{77}As (239.0 keV, not shown), although the latter isotope is almost a pure β^--emitter. It is obvious that a detector with a sufficient energy resolution is required for separating the 559.1 and 564.0-keV peaks. The interference by the ^{76}As 562.8-keV peak cannot be resolved by the detector, hence a chemical separation of the arsenic is required. After the described separation procedure, this interference is negligible, for its intensity is two orders of magnitude lower than that of the 559.1-keV peak of the same isotope. It is obvious from the γ-spectrum that when the 602.7-keV peak of the longer-lived ^{124}Sb isotope is used, the energy resolution of the detector is again a prime consideration.

The results of the ^{122}Sb determinations are summarized in Table II. The antimony contents found in three samples from the same batch are in satisfactory agreement, in view of the low activities involved (average 25 ± 4 p.p.b.). They fall in the same concentration range found by other authors[4,6,7].

It has been found experimentally[1] that the self-shielding in 1-g powdered selenium samples (σ_{abs} = 11.8 barns for thermal neutrons) amounts to *ca.* 4%, in

TABLE II

RESULTS

Sample	*Weight (g)*	*Yield (%)*	*Waiting time (h)*	*Counting time (min)*	*Counts*[a] *564 keV*	*Result for Sb*[a] *(p.p.b.)*
Se 1	1.015	85.0	153.5	1296	572 ± 55	26 ± 3
Se 2	1.032	96.5	173.5	900	430 ± 45	29 ± 3
Se 3	1.027	89.5	221.5	1800	307 ± 55	21 ± 4
Sb 1	$1.41 \cdot 10^{-3}$	100	173.16	5	132 500 ± 400	$(1.21_5 \pm 0.06)$ $\times 10^6$ c/h/mg Sb
Sb 2	$1.73 \cdot 10^{-3}$	100	188.75	5	124 100 ± 400	

[a] Standard deviation based upon counting statistics.

agreement with calculated values. The self-shielding in 1–2 mg of antimony ($\sigma_{abs} = 5$ barns) as powdered oxide is negligible. Hence the results reported in Table II for selenium grains may be too low by *ca.* 4%.

For a 3-h irradiation of a 1-g selenium sample at $7 \cdot 10^{11}$ n cm^{-2} s^{-1}, the detection limit is estimated at *ca.* 5 p.p.b. antimony, when counting with a Ge(Li) detector for 15 h after 1 week. Increase of the neutron dose will lower the counting time and increase the sensitivity, since the main limiting factor is the background activity, as appears from comparing Fig. 1a and 1b. This would of course result in handling a higher matrix activity. In the present irradiation conditions, the ^{75}Se activity amounted to $5 \cdot 10^{-5}$ Ci only.

The authors are grateful to Prof. J. Hoste for his continuous interest and to Miss J. Zels and Miss M. Helsen for technical assistance.

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SHORT COMMUNICATION

A method for the neutron activation analysis of natural waters for arsenic

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(Received 8th May 1972)

The sensitivity of arsenic to neutron activation analysis makes this a desirable technique for determining the arsenic concentration of natural waters. For arsenic concentrations which are $\leqslant 1$ p.p.b., neutron activation can provide adequate precision where other methods often cannot. In sea water, however, the high concentration of other salts relative to arsenic virtually requires that either pre-irradiation chemistry or post-irradiation separations be performed to eliminate the activity from ^{24}Na, ^{38}Cl, and other highly radioactive species. Pre-irradiation chemistry, while increasing the possibility of contamination, does have the advantage that it can be done in the field. Immediate processing of freshly collected samples eliminates some significant sample storage problems which will be discussed in a later section.

The co-crystallization of arsenic with thionalide (α-mercapto-N-2-naphthylacetamide) in low pH aqueous media[1] was used by Portmann and Riley[2] to concentrate arsenic for subsequent colorimetric analysis. In the present paper their procedure is adapted and the thionalide–arsenic precipitate is subjected directly to activation by thermal neutrons. ^{76}As activity is determined by γ-ray spectroscopy methods and calibration is accomplished by standard addition. The technique is applicable to a variety of fresh and salt waters.

The reagents and procedure are those listed by Portmann and Riley with only minor modification. The modified procedure is described below for completeness.

Recommended procedure

Add 1 ml of ascorbic acid solution (5% (w/v); keep frozen, thaw for use) to 250 ml of sample in a 600-ml beaker or Erlenmeyer flask and cover with a watch glass. (A larger volume, with proportionately more reagents, might be used for very low arsenic levels.) Bring the sample just to boiling on a hot plate, then remove and allow to cool for 10 min. Add a further 0.5 ml of the ascorbic acid and cool to room temperature.

Add, while stirring with a magnetic stirrer, 10 ml of 2.5 *M* sulfuric acid, followed by 2 ml of fresh thionalide solution (2% (w/v) solution in acetone). Stir for 5 min, and then leave for 10 min before bringing up to a *gentle* boil on a hot plate. Boil very slowly for 30 min to remove all the acetone, then remove from the heat and allow to cool overnight (8 h is sufficient).

Filter the samples onto 25-mm HAWP 0.45 μm pore-size Millipore filters with a 15-ml chimney. Do not let the filter become dry before filtration is complete or plugging of the filter may cause excessive filtering time. Rinse with 300 ml of deionized water, washing down the chimney with the last 30–40 ml.

Fold the wet filter into a small square and press it into the bottom of an acid-washed 0.5 dram (12 × 23 mm) polyethylene vial. Add 6 drops of acetone to consolidate the filter and precipitate, then evaporate off the acetone at 50°. Alternatively, the samples may be pelletized.

Seal the vials and irradiate with appropriate flux monitors for 7 h in a neutron flux of 4×10^{12} n cm^{-2} sec^{-1}. After cooling overnight, count the ^{76}As activity of the 0.559-MeV peak on a γ-ray spectrometer. In many samples arsenic appears as the middle peak of a ^{82}Br ($t_{\frac{1}{2}}=35.3$ h), ^{76}As ($t_{\frac{1}{2}}=26.5$ h), ^{122}Sb ($t_{\frac{1}{2}}=67.2$ h) triplet requiring the resolution of a Ge(Li) detector for analysis. Since ^{76}As has the shortest half-life of the three, it is advantageous to count as soon as possible after irradiation. A 12-h cooling period before counting is sufficient to allow Compton and Bremsstrahlung effects from highly radioactive species to decay.

Blanks made with deionized water should be run simultaneously through the whole procedure.

Discussion

Tracer studies were made with ^{74}As to determine the optimal pH for co-crystallization. Low pH values were found to be the most advantageous. At pH values of 1.2 and 0.7 (corresponding to an addition of 2.5 and 10 ml, respectively, of 2.5 *M* sulfuric acid to 250 ml of the sample solution) the recovery averaged 95%. This agreed well with the recovery reported by Portmann and Riley.

Numerous blank determinations were made. The values ranged from 0.000 to 0.012 μM arsenic, with a mean value of 0.003 μM. Irradiation of the Millipore filters and vials only showed no detectable ^{76}As activity, but did show some ^{82}Br activity.

To evaluate the accuracy of the method, samples of both deionized and sea water at different added arsenic concentrations were analyzed by the activation method and also by a spectrophotometric method[3]. The results are shown in Fig. 1. The slope of the regression, fitted by least squares, was 1.028 ± 0.03 (standard deviation), showing that over the concentration range examined, the two methods give the same results within experimental error. The correlation coefficient was 0.99.

The accuracy was also judged by a series of standard additions of arsenic to deionized water and to sea water. These results are shown in Table I. The mean deviation of the "found" values from the "added" values was +0.002 μM As.

The precision was estimated from a series of 25 duplicate analyses covering a concentration range from 0.000 to 0.2 μM arsenic. Standard deviations for duplicates were estimated by the method of Dean and Dixon[4]. When expressed as a coefficient of variation (one standard deviation divided by the mean value), the mean value for these duplicates was 8%. These samples were counted for only 100 s. A significant improvement in precision could be obtained with longer counting times.

Several types of natural waters were analyzed by this method including rain water, estuarine water, sea water, and tap water. Some results are shown in Table II. Samples which were stored before analysis have not been reported, because of storage problems.

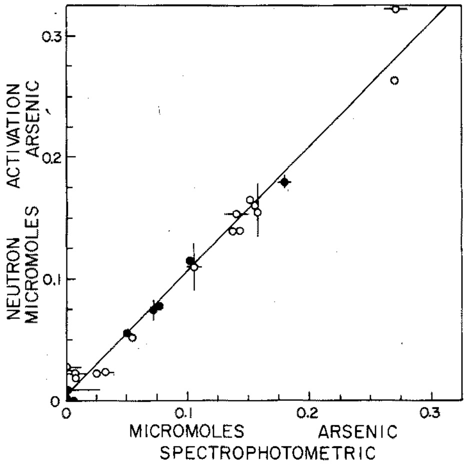

Fig. 1. Comparison of added arsenic concentration obtained by neutron activation analysis and spectrophotometry. Error bars, where present, represent an estimate of one standard deviation. (○) Salt water; (●) fresh water.

TABLE I

RECOVERY OF STANDARD ADDITION OF ARSENIC TO DEIONIZED WATER AND SEA WATER

Sea water		*Deionized water*	
Added (μM)	*Found* (μM)	*Added* (μM)	*Found* (μM)
0.026	0.031 ± 0.002[a]	0.053	0.056 ± 0.003[a]
0.080	0.088 ± 0.021	0.066	0.075 ± 0.009
0.130	0.124 ± 0.012	0.079	0.078 ± 0.004
0.130	0.130 ± 0.013	0.106	0.116 ± 0.004
0.132	0.134 ± 0.020	0.185	0.180 ± 0.005
0.263	0.261 ± 0.029		

[a] Analytical uncertainties, estimated from replicate determinations, represent one standard deviation.

Notes on sample storage

Samples collected at sea for later analysis by the activation technique described here were preserved by the addition of 9 ml of concentrated hydrochloric acid per liter of sample and stored in 1-l acid-washed polyethylene bottles. This procedure, while adequate for many trace elements, does not appear to work for arsenic. Analyses for total arsenic by spectrophotometry at the time of sample collection showed that sea water samples thus preserved lost up to 70% of their arsenic content. This loss occurred within one week and was determined by both activation analysis and spectrophotometry (which confirmed each other). By analogy with Robertson's work[5] on antimony, such a loss was not expected. Appropriate studies with radioactive tracers are needed to develop adequate sample storage techniques.

TABLE II

ARSENIC CONCENTRATIONS IN NATURAL WATERS

Date	*Sample*		*Arsenic (μM)*[a]
23(XI)'72	Rain (at Narragansett Marine Lab.)		0.011 ± 0.002
24(XI)'71	Narragansett Bay water	(1)	0.022 ± 0.002
11(III)'72	Narragansett Bay water	(2)	0.021
24(XI)'71	Narrow River water		0.012 ± 0.001
23(X)'71	Sargasso Sea water (stored in plastic)		0.022 ± 0.003
11(III)'72	N.M.L. tap water		0.004 ± 0.001
10(III) '72	Providence tap water		0.006 ± 0.010
10(III)'72	Providence River	(1)	0.012 ± 0.004
10(III)'72	Providence River	(2)	0.010 ± 0.001
10(III)'72	Seekonk River	(1)	0.046 ± 0.004
10(III)'72	Seekonk River	(2)	0.033 ± 0.006

[a] Analytical uncertainties, estimated from replicate determinations, represent one standard deviation.

We wish to thank the reactor staff at the Rhode Island Nuclear Science Center for providing space and facilities for these analyses.

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SHORT COMMUNICATION

Determination of inorganic mercury in natural waters

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Several workers[1-3] have used a potassium permanganate–sulphuric acid solution as a trapping solution for mercury in air. Considerable work[4-11] has also been done on the determination of mercury in solution by flameless cold vapour atomic absorption. This communication describes a procedure, incorporating both techniques, which has recently been developed and used in this laboratory for the determination of mercury in sea waters enriched with mercury at levels of 0.1, 1.0 and 10.0 μg l^{-1} as part of studies on the effects of sublethal amounts of trace metals on marine food chains. The technique described below permits water samples to be analysed for mercury down to 0.002 μg l^{-1}, with a 4-l sample. Scale expansion is not required, so that an extremely steady base line on the chart record is ensured.

Experimental

Apparatus. The instrument used was a Varian Techtron model AA120 atomic absorption spectrophotometer equipped with a Servoscribe recorder (RE511) and a 15-cm gas cell with silica windows. Operating conditions are given in Table I.

TABLE I

ATOMIC ABSORPTION CONDITIONS

Source	Hollow-cathode lamp
Slit	100 μm
Lamp current	3 mA
Wavelength	253.65 nm
Scale expansion	1 ×
Chart speed	30 mm min^{-1}

Reagents and preparation. All chemicals were reagent grade. Solutions were prepared with deionized water. The solution used for absorbing mercury from the stream of air was prepared by mixing equal volumes of 2% (w/v) potassium permanganate solution and 50% (v/v) sulphuric acid. The tin(II) chloride solution (20% w/v) used to reduce the permanganate and liberate the mercury was prepared in 5 *M* hydrochloric acid. Before use, this solution was aerated for *ca.* 1 h to remove the traces of mercury in both the reagent and the acid.

Mercury solutions. A 1,000 p.p.m. stock standard solution of mercury, as $HgCl_2$ (Hopkin and Williams Ltd., Chadwell Heath, Romford) was used for the preparation of substandards by suitable dilution. In the calibration procedure, 1 ml of the absorption solution was used to each 100 ml of diluted standard solution[10]. All glassware was washed with several small volumes of the absorption solution and then rinsed with deionized water.

Concentration apparatus. Air (600 $cm^3\ min^{-1}$) from a small electric pump was passed into a large aeration vessel (glass bottle—5 l) through an air stone of coarse porosity. The outlet from this vessel was connected to an absorption cell, consisting of a ground-glass stoppered absorption head and test tube (*ca.* 75 ml), and containing 20 ml of permanganate–sulphuric acid solution. All connections were made with polyethylene tubing.

Procedure

Transfer 4 l of the sea water sample to the glass container and add 45 ml of the tin(II) chloride solution, quickly replacing the rubber bung carrying the diffuser head. Secure all connections (as described above), pipette 20 ml of the absorption solution into the test tube and switch on the air supply. Allow the aeration to proceed for 5 h. (This aeration time, although lengthy, is convenient for laboratory staff operating on board ship and in the shore laboratory. Should this length of time be found inconvenient, the conditions of temperature and air flow can be altered (see Table II) to reduce the aeration time to 30 min and still achieve complete recovery of mercury from the sample.)

TABLE II

THE EFFECT OF TEMPERATURE ON THE RECOVERY OF 0.50 μg OF MERCURY ADDED TO 4 l OF SEA WATER

Rate of aeration ($cm^3\ min^{-1}$)	*Temp* (°)	*Mercury found*[a] (μg)	
		Aeration time 15 *min*	*Aeration time* 30 *min*
600	20	0.06, 0.06	0.14, 0.15
	50	0.19, 0.21	0.30, 0.33
	80	0.22	0.36
1500	20	0.26	0.30
	50	0.26	0.36
	80	0.49	0.51

[a] Corrected for mercury in air supply.

Disconnect the air supply, transfer the contents of the test tube together with necessary washings to a 100-ml Drechsel wash bottle and make up to the 50-ml mark. Add 15 ml of tin(II) chloride solution, quickly replace the Drechsel head and mix well. Aerate the sample (2 l min^{-1}) and conduct the air+mercury vapour through the gas cell. Record the peak deflection height.

Calibration. To test tubes containing 20 ml of absorption solution add 0.2, 0.4, 0.6, 0.8 and 1.00 ml of a freshly prepared 1 μg ml^{-1} mercury standard solution.

Transfer each solution and washings made up to a volume of 50 ml to the 100-ml wash bottle and repeat the relevant stages of the procedure described above.

Results and discussion

To evaluate the method, synthetic standards were prepared by spiking samples of pre-aerated sea water (2–10 l) with known quantities of standard mercury solution. The results are given in Table III. Experiments were carried out to assess the effect of varying (*a*) aeration time, and (*b*) rate of aeration. The results are given in Table IV. Background mercury levels in the atmosphere of the laboratory should be checked by aerating 20-ml samples of absorption solution for 5-h periods. If the air supply contains significantly high levels of mercury, a clean-up operation should be employed before the aeration stage. This can best be achieved by passing the air through two absorption tubes, in series, containing 20 ml of the absorption solution and a distilled water wash respectively. Samples of water should be analysed as soon as possible after collection to avoid losses of mercury by adsorption on to the walls of the container. Samples to be stored for periods longer than 12 h should be spiked with suitable

TABLE III

RECOVERY OF MERCURY ADDED TO VARYING VOLUMES OF SEA WATER

Volume of sample (*l*)	*Mercury added* ($\mu g\ l^{-1}$)	*Mercury found*[a] ($\mu g\ l^{-1}$)
2	2.0	1.96
2	1.0	0.97
2	0.50	0.49
4	0.50	0.51
4	0.50	0.52
10	0.20	0.20
10	0.20	0.20

[a] Corrected for mercury in air supply.

TABLE IV

THE EFFECT OF AERATION TIME AND RATE OF AERATION ON RECOVERY OF 1 μg OF MERCURY ADDED TO 4 l OF SEA WATER

Aeration rate ($l\ h^{-1}$)	*Aeration time* (*h*)	*Mercury found* (μg)	*Corrected mercury*[a] *value* (μg)
36	1	0.60	0.59
	3	0.98	0.95
	5	1.05	0.99
72	1	0.87	0.85
	3	1.04	0.98
	5	1.09	0.99
108	1	0.96	0.93
	3	1.08	0.99
	5	1.13	0.97

[a] Corrected for mercury in air supply.

volumes of absorption solution (20 ml l^{-1} of sample) to avoid such losses. (Under these conditions, according to Omang[10] and experiments conducted in this laboratory, any organic mercury present as methyl mercury will be decomposed to the inorganic state.) After addition of suitable quantities of tin(II) chloride solution to neutralise the potassium permanganate, the samples can then be analysed as described above.

During a recent cruise of FRS "Explorer" several samples of sea water were collected and "concentrated" as described above. Final analysis was carried out on return to the shore-base laboratory. Levels of mercury in the range 0.008–0.055 $\mu g\ l^{-1}$ were found (Table V); these levels are similar to those obtained for samples collected from the North Sea[12], the English Channel[13] and the N.E. Atlantic Ocean[14].

The results to date have shown that this relatively simple technique can be used successfully, under field conditions, for the determination of extremely low mercury levels in natural waters.

TABLE V

CONCENTRATION OF MERCURY FOUND IN SEA WATER SAMPLES COLLECTED FROM THE NORTH SEA AT 5 m DEPTH

(April 1972, FRS "Explorer")

Position		*Hg found* (*$\mu g\ l^{-1}$*)	*Position*		*Hg found* (*$\mu g\ l^{-1}$*)
57°54'N 02°06.5'W	Moray Firth	0.010	60°04.7'N 00°34'E	Orkney–Shetland	0.020
57°46.5'N 03°24.5'W		0.010	60°57.5'N 00°25'E	area	0.010
			60°42.5'N 00°38'W		0.011
58°03.5'N 02°59.5'E	northern	0.010	59°33.5'N 01°16.5'W		0.010
58°35'N 00°13'E	North Sea	0.055	58°51.5'N 02°26.5'W		0.008
59°16'N 01°03.5'E		0.020			
58°36.8'N 01°21.4'W		0.055			
57°23.5'N 01°16'W		0.030			

The authors would like to thank Mr. Norman Michie for his assistance in these experiments, and Dr. R. Johnston for collecting and treating the North Sea samples.

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SHORT COMMUNICATION

Spectrophotometric determination of zirconium in nickel-base alloys with arsenazo III after thenoyltrifluoroacetone extraction

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The use of high-temperature alloys as a heat exchanger for a multi-purpose high-temperature gas-cooled reactor is being investigated at the Japan Atomic Energy Research Institute. In this program, a method was needed for determining 0.01–0.1% of zirconium in nickel-base alloys.

Zirconium in nickel-base alloys has been determined with xylenol orange after electrolysis with a mercury cathode and sodium hydroxide precipitation[1]. This method has been further developed for the separate and simultaneous determination of zirconium and hafnium in nickel-base alloys[2].

Because of its high sensitivity and selectivity, the use of arsenazo III for the determination of zirconium in nickel-base alloys has been studied. In previous work[3], zirconium was separated from thorium by thenoyltrifluoroacetone (TTA) extraction before its determination with arsenazo III. The present work has demonstrated that this approach is also useful for the determination of more than 0.01% of zirconium in nickel-base alloys. While this work was in progress, Pakalns[4] described a method for the determination of zirconium in steels with arsenazo III. In his method, zirconium is separated by precipitation with cupferron; thorium, if present, interferes. The TTA extraction from *ca.* 4 *M* hydrochloric acid solution, however, provides for the presence of thorium.

Experimental

Standard zirconium solution. A stock solution, containing 1.00 mg ml^{-1} of zirconium, was prepared by dissolving 3.533 g of $ZrOCl_2 \cdot 8H_2O$ in 2 *M* hydrochloric acid, and diluting to exactly 1 l with 2 *M* hydrochloric acid. This solution was standardized by titration with ethylenediaminetetraacetic acid disodium salt, with xylenol orange as indicator[5]. A working standard solution was prepared by diluting the stock solution with 2 *M* hydrochloric acid.

Apparatus. Absorbance measurements were made with a Hitachi Model 139 spectrophotometer, in 1-cm cells. A shaking machine was used for extractions.

Procedure. Dissolve 100 mg of sample by heating with a mixture of 10 ml of concentrated nitric acid, 10 ml of concentrated hydrochloric acid, and 10 ml of water. Transfer the solution to a 50-ml volumetric flask and dilute to volume with water. Transfer a suitable aliquot (1–10 μg Zr) of the solution to a beaker and evaporate the solution to about 1 ml. Dilute the solution with 20 ml of 4 *M* hydrochloric acid and transfer to a 100-ml separatory funnel. Add 50 mg of ascorbic acid and 10 ml of 0.5 *M* TTA in xylene and shake for 10 min. When the layers have separated, drain off and discard the aqueous phase. Wash the organic phase by shaking it for 10 min with 10 ml of 4 *M* hydrochloric acid and discard the aqueous phase. To the organic phase add 10 ml of a 0.2 *M* hydrofluoric acid–0.2 *M* nitric acid mixture and shake for 3 min to back-extract zirconium. Transfer the aqueous phase to a 100-ml Teflon beaker. Shake the organic phase for 30 s with 3 ml of 0.2 *M* hydrofluoric acid–0.2 *M* nitric acid. Add the aqueous phase to the same beaker and evaporate to dryness on a hot plate with the aid of an infrared lamp. (Discard the organic phase.) To the residue add 1 ml of concentrated nitric acid, 1 ml of 60% perchloric acid, and 1 ml of water and transfer the solution to a platinum dish. Evaporate the solution to dryness.

Dissolve the residue in 10 ml of concentrated hydrochloric acid. Transfer the solution to a 25-ml volumetric flask, wash the dish with 8.5 ml of concentrated hydrochloric acid, add 1.0 ml of aqueous 0.1% (w/v) arsenazo III solution, and dilute to the mark with water. Measure the absorbance of the solution in a 1-cm cell at 665 nm using water as the reference. Run a blank through the entire procedure.

Construct a calibration curve by taking, for example, 0, 2.0, 6.0, and 10 μg of zirconium and carrying them through the entire procedure.

TABLE I

EFFECT OF OTHER IONS ON THE SEPARATION AND DETERMINATION OF ZIRCONIUM

(Zr taken: 6.0 μg)

Ions added						*Zr found (μg)*
Ni,		10 mg				6.2, 6.1
Ni,		30 mg				5.9, 5.8
Ni,		50 mg				5.5, 5.6
Ni,	10 mg;	Cr(III),	2 mg;	Fe(III),	1 mg	5.9, 6.0
Ni,	30 mg;	Cr(III),	6 mg;	Fe(III),	3 mg	5.8, 6.0
Ni,	10 mg;	Cr(III),	2 mg;	Fe(III),	1 mg	6.0, 6.0
U(VI),	5 μg;	Th,	5 μg;	Dy,	5 μg	

TABLE II

ANALYSIS OF STANDARD SAMPLES

Sample	*Zr present (%)*	*Zr found (%)*				*Average Zr found (%)*
NBS 1203, Inco 713-A[a]	0.055	0.053, 0.052,	0.053, 0.053,	0.054, 0.052		0.053
NBS 1204, Inco 713-B[b]	0.12	0.12,	0.12,	0.11,	0.11	0.12

[a] NBS 1203 contains Mn, 0.31%; Si, 0.86; Cu, 0.19; Ni, 75.5; Fe, (1.4); Cr, 11.90; Mo, 3.01; W, <0.01; Al, 4.34; Ti, 1.09; Nb, 1.00; Ta, 0.34%.

[b] NBS 1204 contains Mn, 0.41%; Si, 0.56; Cu, 0.12; Ni, 70.6; Fe, (3.1); Cr, 12.75; Mo, 4.28; W, 0.028; Al, 5.60; Ti, 0.63; Nb, 1.31; Ta, 0.46%.

Results and discussion

From the calibration curve constructed without TTA extraction a molar absorptivity of $1.36 \cdot 10^5$ l mol^{-1} cm^{-1} was obtained. From the calibration curve involving extraction a molar absorptivity of $1.29 \cdot 10^5$ was obtained. Therefore, the recovery of zirconium was about 95%. Double extraction with 10 ml and 5 ml of TTA did not appreciably improve the recovery.

The effect of the matrix elements (Ni, Cr, and Fe) and uranium, thorium and dysprosium on the analysis for zirconium is shown in Table I. Nickel (30 mg), chromium (6 mg), and iron (3 mg) did not interfere with the separation and determination of 6 μg of zirconium. Low results were obtained with 50 mg of nickel. Zirconium (6 μg) was added to 10 mg of a nickel-base alloy that did not contain an appreciable amount of zirconium. The percentage composition of the alloy was: C, 0.04; Si, 0.3; Mn, 0.7; Ni, 72; Cr, 15; Fe, 6.3; Cu, 0.03; Al, 0.7; Co, 0.5; Ti, 2.8; and Nb, 1. The analysis of this sample for zirconium gave 6.1 and 6.0 μg.

The proposed method was applied to National Bureau of Standards (NBS) high-temperature alloy samples (Table II). From the results, it may be concluded that elements present in these samples do not interfere in the proposed method. Six analyses of NBS 1203 sample gave a relative standard deviation of 1.3%. In the present work, hafnium that may be present with zirconium was not considered.

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SHORT COMMUNICATION

Spectrophotometric determination of uranium in selective organic extractants with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol

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(Received 6th June 1972)

In many uranium processing plants, uranium is purified by extraction with tributyl phosphate (TBP) or long-chain tertiary amines such as Alamine-336 (tricaprylmethylammonium chloride). It would be convenient to determine uranium directly in the organic phase without having to resort to acid stripping or destruction of the organic solvent. While milligram amounts of uranium in these extractants can be readily determined by titration with potassium dichromate[1], determination of smaller amounts is more difficult. To use fluorimetry for these levels of uranium, the organic sample has to be diluted with kerosene.

A new, highly sensitive reagent, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (bromo-PADAP) has recently been described for the spectrophotometric determination of uranium in ores and waters[2]. It was found that dimethylformamide forms a single phase with water, kerosene, ethanol, and TBP or Alamine-336. By this means it was possible to determine uranium directly in the extracts.

Apparatus and reagents

Unicam SP600 spectrophotometer with 1- and 4-cm glass cuvettes.

Standard uranium solution, 1 *mg ml*$^{-1}$. Dissolve 0.1792 g of pure U_3O_8, ignited at 900°, in 20 ml of 2.5 *M* nitric acid, and dilute to 100 ml with water. Prepare 10, 20, 40 and 50 μg U ml^{-1} standard solutions from this stock solution by dilution.

Complexing solution. Suspend 12.5 g of CyDTA (Fluka), 2.5 g of sodium fluoride and 32 g of sulphosalicylic acid in 800 ml of water. Neutralize to pH 7.45 with 40% sodium hydroxide and dilute to 1 l.

Buffer solution, pH 7.45. Dissolve 300 g of triethanolamine in 700 ml of water, neutralise to pH 7.45 with perchloric acid and allow to stand overnight. Readjust to pH 7.45 with perchloric acid and dilute to 1 l.

Alamine 336 (General Mills Chemical Division, Kankakee, Ill.), reagent-grade tributyl phosphate and domestic kerosene ("odourless") were used.

Recommended procedure

20% *TBP–kerosene.* Pipette an aliquot (2 ml maximum) of the 20% TBP–kerosene extract containing less than 150 μg of uranium into a 50-ml volumetric flask. (If the sample is strongly acidic, determine on a separate aliquot the volume of 10% sodium hydroxide required for neutralization by adding 20 ml of water and using 5 drops of 0.04% bromocresol green indicator.) Add water, 3 ml less the volume required to neutralize the sample. Then add 1.00 ml of complexing solution, 2.00 ml of buffer solution, the volume of 10% sodium hydroxide required for neutralization, 10 ml of dimethylformamide (>99% pure) and 20 ml of absolute ethanol. Add 4.00 ml of ethanolic 0.05% bromo-PADAP solution, dilute to volume with absolute ethanol and mix for at least 30 s. Allow to stand for 20 min and then measure the colour at 578 nm against a reagent blank containing an equivalent amount of 20% TBP–kerosene. Use 1-cm cells for 15–150 μg U and 4-cm cells in the 1–15 μg range. With a 1-cm cell 100 μg of uranium gives an absorbance of 0.60.

Prepare a standard by pipetting an amount of 20% TBP–kerosene equivalent to that taken for the sample into a 50-ml volumetric flask. Add 3.00 ml of uranium standard, 1.00 ml of complexing solution and continue as in the recommended procedure.

5% *Alamine-336–kerosene.* Pipette an aliquot of the Alamine-336–kerosene extract, 1.0 ml or less, and containing less than 7.5 mg of sulphate and less than 150 μg of uranium, into a 50-ml volumetric flask. Determine the volume of 10% sodium hydroxide required for neutralization. Add 1 ml of thorium solution (3 mg Th ml^{-1} prepared from thorium nitrate) and water (2 ml less the volume required to neutralize the sample). Continue as in the case of 20% TBP–kerosene, except that the standard curve is prepared with 2.00 ml of uranium standard solutions.

Discussion

Although butyl cellosolve is one of the best solvents for forming a single phase with water, TBP and kerosene[3], no colour developed between bromo-PADAP and uranium in the presence of this solvent. Dioxane was found to be suitable but the colour of the uranium–bromo-PADAP complex was only 80% of that obtained by using dimethylformamide; 10 ml of dimethylformamide was sufficient to form a single phase with 2 ml of 20% TBP–kerosene, 3 ml of water, 2 ml of 30% triethanolamine buffer, 1 ml of complexing solution and 32 ml of absolute ethanol. The pH range for maximal absorbance of the final spectrophotometric solution was 6.6–7.43. The addition of 0.15 ml of 2.5 *M* sodium hydroxide or 0.3 ml of 2.5 *M* hydrochloric acid to the working solution did not change the absorbance.

A single phase with 10 ml of dimethylformamide is only formed with a maximum amount of 1.6 ml of kerosene; therefore, if kerosene solutions containing less than 20% TBP are used, the sample size must not exceed 1.6 ml.

The molar absorptivity of the uranium–bromo-PADAP complex in the presence of 2 ml of 20% TBP–kerosene or 1 ml of 5% Alamine-336–kerosene solutions is $7.03 \cdot 10^4$ which is similar to that obtained in TOPO extracts[2]. The complex exhibits maximal absorbance between 575 and 580 nm. The absorbance can be measured 20 min after mixing; on standing for a further 20 min the absorbance increases by only 0.4%. The uranium–bromo-PADAP complex in the dimethylformamide–ethanol mixture has a very low temperature coefficient. There was less than 0.3% variation in absorbance in the temperature range 18 to 25°.

The detection limit for uranium measured in 4-cm cells was 0.3 μg of uranium. The relative standard deviation at the 100-μg level of uranium was 0.4%.

Interferences

The mixtures of 20% TBP–kerosene and 5% Alamine-336–kerosene extract uranium(VI) from nitrate and sulphate solutions, respectively, preferentially to many other elements. Therefore the levels of cationic impurities in the organic phase are at a low p.p.m. level. Because of the small amount of interfering ions present, it was decided to add a minimal amount of the complexing solution, because the complexing agent forms a weak complex with uranium and decreases the colour[4]. Doubling the concentration of the complexing solution decreased the absorbance by 5%.

The following elements caused less than ±2% error in the determination of 100 μg of uranium: 200 mg of $NaNO_3$, $NaClO_4$ and NaCl; 5 mg of SO_4^{2-}; 1 mg of Bi(III), Ca, Cd, Co, Cu, Ge, Hg, Fe(III), La, Mg, Mn, Mo, Ni, Pb, Si, Sb(III), Sn(II), Th, W and Zn; 0.5 mg of Ti and Zr; 0.25 mg of As and Be; 100 μg of Al, Ce(IV) and Cr(III); 150 μg of PO_4^{3-}; 15 μg of V(V). The only serious interference was caused by sulphate ion which, in the absence of thorium, must be below 5 mg because 7.5 mg of sulphate gave results low by 40%. It was found that 1 ml of 5% Alamine-336–3% nonanol–kerosene mixture extracted *ca.* 7 mg of sulphate. To complex this amount of sulphate, 3 mg of thorium was added to the sample solution, but even then 10 mg of sulphate produced an error of −4%. When extraction mixtures containing more than 5% Alamine-336 in kerosene are analysed, a smaller sample must be taken so as not to exceed 7.5 mg of sulphate per sample aliquot.

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SHORT COMMUNICATION

Determination of traces of formaldehyde, glyoxylic and glycollic acids in acetic acid–water mixtures

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In the determination of very low concentrations (10^{-6}–10^{-7} *M*) of formaldehyde, glyoxylic and glycollic acids in acetic acid–water mixtures, the presence of large amounts of acetic acid must be taken into account. The following three reagents, none of which react with acetic acid, were therefore selected: 2-hydrazinobenzothiazole[1] for formaldehyde, phenylhydrazine hydrochloride[2] for glyoxylic acid, and 2,7-dihydroxynaphthalene[3] for glycollic acid. The literature data showed that these methods were insufficiently sensitive for the required purpose, so a systematic investigation was made to improve the sensitivity. A modified procedure, for radiation chemical experiments, similar to those performed for determination of acetone, acetaldehyde and methyl acetate in acetic acid[4] was developed; good results can be achieved in a wide range of acetic acid concentrations.

Experimental

Apparatus and reagents. A Unicam SP 500 spectrophotometer with 10, 20 and 40-mm optical cells was used for absorption measurements. Where possible, analytical reagent-grade chemicals were used.

Determination of formaldehyde. Formaldehyde was determined with 2-hydrazinobenzothiazole, a sufficiently selective reagent for aliphatic aldehydes. Glycollic acid does not react, while the effect of glyoxalic acid is negligible ($A^{1\%}_{1\,\mathrm{cm}}=400$)*, and formaldehyde could be determined in the presence of acetic acid with no significant change in percentage absorptivity, provided that a suitable amount of potassium hydroxide solution was used in the procedure (Table I), to obtain the optimal conditions for colour development.

The recommended procedure, with lower dilution factor, is as follows. Mix 2.5 ml of test solution and 1 ml of aqueous 0.5% reagent solution and leave for 5 min. Then add 1 ml of 1% hexacyanoferrate(III) solution and, after 15 min, 1 ml

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* For the purpose of comparing results for different components in mixtures, $A^{1\%}_{1\,\mathrm{cm}}$ values are given (percentage absorptivity); the values were calculated from the formula $A_m = A^{1\%}_{1\,\mathrm{cm}}\,lc$, where A_m is the absorbance measured, l the cell length, and c the initial concentration in percentage by weight of the substance measured.

TABLE I

AMOUNTS OF 20% POTASSIUM HYDROXIDE SOLUTION USED IN THE DETERMINATION OF FORMALDEHYDE WITH 2-HYDRAZINOBENZOTHIAZOLE IN ACETIC ACID–WATER MIXTURES

CH_3COOH (M)	0	0.1	1	5	10	15–17
KOH (ml): f_{10}[a]	0.5	0.5	1	2	2	3
f_4	0.5	1.0	1.5	4	–	–

[a] *f* is the dilution factor, *i.e.* proportion of final volume to test solution volume.

of dimethylformamide. Dilute to 10 ml with water and measure the absorbance against a blank containing 2.5 ml of acetic acid solution. The procedure is applicable to acetic acid concentrations up to 5 *M*; higher concentrations interfere.

Determination of glyoxylic acid. Both glyoxylic acid and formaldehyde react with phenylhydrazine hydrochloride. As the method with 2-hydrazinobenzothiazole determines only formaldehyde, combining these two methods makes it possible to determine glyoxylic acid alone. When the percentage absorptivities for the two compounds had been established, this procedure was shown to be valid within experimental error. Good results were obtained when the method was applied to pure acetic acid and its solutions.

The following somewhat modified procedure decreases the dilution factor (from 4 to 2.5). Mix 4 ml of test solution and 0.8 ml of 5% reagent solution, and heat for 5 min at 110°. Allow to cool to room temperature, add 2.5 ml of concentrated hydrochloric acid and 2.5 ml of 1% hexacyanoferrate (III) solution and dilute to 10 ml with water. Measure the absorbance against a blank containing 4 ml of acetic acid solution or pure acid.

Determination of glycollic acid. To determine glycollic acid, 2,7-dihydroxynaphthalene in concentrated sulfuric acid was used. The concentrated sulfuric acid splits glycollic acid to form formaldehyde[5], hence any formaldehyde present will also be determined. The absorbance measured arises from both glycollic acid and formaldehyde, and the percentage absorptivity is the same for both compounds. The method is applicable to pure acetic acid and its solutions.

The procedure described earlier[3] can be simplified as follows. Heat 0.5 ml of test solution and 5 ml of 0.01% reagent solution in concentrated sulfuric acid for 30 min at 105°. Cool to room temperature, add concentrated sulfuric acid to give a volume of 10 ml, and measure the absorbance against a blank containing 0.5 ml of acetic acid solution or pure acid. The relatively high dilution factor (20) is a disadvantage, but it can be improved by using 4 ml of test solution and 6 ml of 0.01% reagent solution in concentrated sulfuric acid, with the same final volume of solution. When the reagent solution is added to acetic acid concentrations up to 5 *M*, samples should be cooled in water to avoid excessive heat evolution.

Determination of percentage absorptivity. Percentage absorptivities for each of three reactions used above were determined in water, acetic acid–water mixtures and pure acetic acid. For comparison, measurements were performed for two dilution factors; the first corresponds to the procedures developed here and the second to methods found in the literature. The results are listed in Table II. The experimental errors, ±6%, were greater than those usual for spectrophotometric measurements, probably because of the large amounts of acetic acid present. Nevertheless, radiation

TABLE II

EXPERIMENTAL DATA FOR FORMALDEHYDE, GLYOXYLIC AND GLYCOLLIC ACID

Reagent	*Compound*	*Solvent*	$A_{1\,cm}^{1\%} \cdot 10^{-3}$ [a]	*Dilution factor*		*Sensitivity*[b]	
				Present work	*Literature*	1	2
2-Hydrazinobenzothiazole	CH_2O	H_2O; 0.1 *M* CH_3COOH	45.00	4	10	11.25	4.50
		1–5 *M* CH_3COOH	43.00	4	10	10.75	4.30
		10–17 *M* CH_3COOH	36.40	—	10	—	3.64
Phenylhydrazine hydrochloride	CH_2O	H_2O; 0.1–5 *M* CH_3COOH	6.25	2.5	4	2.50	1.56
		10–17 *M* CH_3COOH	4.40	2.5	4	1.76	1.10
	CHOCOOH	H_2O; 0.1 *M* CH_3COOH	24.00	2.5	4	9.60	6.00
		1–17 *M* CH_3COOH	19.00	2.5	4	7.60	4.75
2,7-Dihydroxynaphthalene	CH_2O and $CH_2OHCOOH$	H_2O; 0.1 *M* CH_3COOH	23.00	2.5	20	9.20	1.15
		1–17 *M* CH_3COOH	30.00	2.5	20	12.00	1.50

[a] Mean value for 10–15 determinations.

[b] Sensitivity $= A_{1\,cm}^{1\%} \cdot 10^{-3}/f$.

chemical yields of formaldehyde, glyoxylic and glycollic acids from irradiated acetic acid–water mixtures could be determined by the proposed methods with experimental errors of less than ±10%. As the concentrations determined were at the lower limit of, or even below, the Beer's law range, and as errors in the formaldehyde determination accumulate in the final figures for glyoxylic and glycollic acid, the results can be considered satisfactory.

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SHORT COMMUNICATION

Determination of oxybarbiturates by low-temperature luminescence measurements

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The widespread use and abuse of barbiturates has stimulated the development of many methods for their detection and assay. Ultraviolet spectrophotometry and thin-layer and gas–liquid chromatography have been the most widely used techniques[1]. Spectrofluorimetric methods, however, are frequently more sensitive, and are feasible with small volumes of very dilute samples: the determination of several barbiturates by room-temperature fluorescence measurements has been described by Udenfriend[2], and very recently by Miles and Schenk[3]. Detection limits as low as 0.1 μg ml^{-1} have been obtained for oxybarbiturates.

Luminescence measurements at liquid nitrogen temperature (77 °K) have recently become feasible[4]. In these conditions, the absence of dynamic quenching may produce an increase in the quantum yield of prompt fluorescence, with a consequent increase in analytical sensitivity, and phosphorescence may also be observed. Winefordner and Tin[5,6] have shown that phenobarbitone (5-ethyl-5-phenylbarbituric acid), mebaral (1-methyl-5-ethyl-5-phenylbarbituric acid) and rutonal (5-methyl-5-phenylbarbituric acid) all exhibit delayed emission at 77 °K and that the sensitivity of analysis based on this luminescence is at least as good as that of a conventional fluorimetric assay.

The present paper reports a comprehensive survey of the luminescence properties of the commonly used oxybarbiturates, both at room temperature and at 77 °K, and describes their determination in whole blood samples. Comparisons of the detection limits obtained confirm that low-temperature measurements will be of value in several cases.

Experimental

Excitation and emission spectra, uncorrected for instrumental characteristics, were obtained with a Baird-Atomic SF100E spectrofluorimeter in conjunction with a Bryans Model 27000 strip recorder, or a Model 21005 X-Y recorder. The manufacturer's phosphoroscope and cell housing were modified so that, for measurements at 77 °K, the quartz sample tube (i.d. 2 mm, wall thickness 1 mm; Thermal Syndicate Ltd., Wallsend) could be rotated at speeds up to 320 rev min^{-1} by a small electric motor[7]. A stream of dry air was blown on to the Dewar flask containing the liquid nitrogen. Room-temperature measurements were performed in 1-cm Spectrosil cells (Optro Ltd., Hornchurch, U.K.) in a conventional housing.

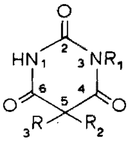
Delayed luminescence lifetimes (>1 s) were determined by observing the decay of the luminescence on the strip recorder after moving a shutter into the exciting light beam. A correction was made for the response time of the system.

Barbiturates were extracted from 5 ml of whole blood samples as described by Broughton[8], except that two back-extractions from chloroform into 0.45 *M* sodium hydroxide were performed. The combined extracts had a total volume of 20 ml, which was increased to 40 ml when ethanediol was added to produce the ethanediol–water (1+1, v/v) solvent for low-temperature work. These dilutions of the original sample volume were allowed for in comparing the detection limits obtained with blood extracts and with pure barbiturate solutions. The detection limit was defined in each case as the concentration of solute yielding a signal which exceeded the background signal by two standard deviations.

The barbiturates studied are listed in Table I. Methylphenobarbitone was obtained from Winthrop Laboratories, methohexitone from Eli Lilly, and heptabarbitone from Geigy. Other samples were obtained from May and Baker, Ltd. All the barbiturates had melting points within 2° of literature[9] values except for butobarbitone (found 118°, literature 127–130°). Solvents for luminescence measurements were purified as follows. Water was distilled three times in an all-silica still,

TABLE I

STRUCTURES OF THE BARBITURATES STUDIED



Compound no.	*Name*	R_1	R_2	R_3
1,5,5-*Substituted*				
1	Hexobarbitone	Methyl	Methyl	Δ'-Cyclohexenyl
2	Mebaral	Methyl	Ethyl	Phenyl
3	Metharbital	Methyl	Ethyl	Ethyl
4	Methohexitone	Methyl	Allyl	1-Methylpent-2-ynyl
5,5-*Substituted*				
5	Rutonal	H	Methyl	Phenyl
6	Phenobarbitone	H	Ethyl	Phenyl
7	Barbitone	H	Ethyl	Ethyl
8	Butobarbitone	H	Ethyl	*n*-Butyl
9	Butabarbitone	H	Ethyl	*sec.*-Butyl
10	Pentobarbitone	H	Ethyl	1-Methylbutyl
11	Amylobarbitone	H	Ethyl	Isoamyl
12	Nealbarbitone	H	Neo-pentyl	Allyl
13	Quinalbarbitone	H	1-Methylbutyl	Allyl
14	Cyclobarbitone	H	Ethyl	Δ'-Cyclohexenyl
15	Heptabarbitone	H	Ethyl	Δ'-Cycloheptenyl

and ethanediol (British Drug Houses Ltd.) was stored under nitrogen and used without further purification. All other reagents were Analar or equivalent grade.

Results

Table II summarizes the detection limits of the barbiturates at room temperature for solutions obtained by dissolving the pure solids in aqueous 0.1 *M* sodium hydroxide; similar data resulted when 0.1 *M* sodium hydroxide in ethanediol–water (1+1, v/v) was used as solvent. The fluorescence of N-methyl barbiturates (compounds 1–4, Table I) was very feeble, being of comparable intensity to the solvent Raman emission. All the other compounds showed broad featureless fluorescence spectra, $\lambda_{ex}=276$–278 nm, $\lambda_{fl}\simeq 420$ nm, with sufficient intensity to permit their determination at microgram or submicrogram concentrations. Fluorescence intensity–concentration plots were linear up to solute concentrations of at least 30 μg ml^{-1} in the final solution.

In Table III the luminescence properties of the barbiturates at 77 °K in the ethanediol–water solvent are listed.

TABLE II

ROOM-TEMPERATURE FLUORESCENCE OF OXYBARBITURATES IN AQUEOUS 0.1 *M* SODIUM HYDROXIDE

Compound[a,b]	5	6	7	8	9	10
Detection limit (μg ml^{-1})	1.5	1.5	0.1	0.1	0.1	0.05
Compound	11	12	13	14	15	
Detection limit (μg ml^{-1})	0.1	1.0	1.0	1.0	3.0	3.0

[a] See Table I.

[b] The excitation wavelength was 278 nm for compounds 5,6; 277 nm for compounds 7, 12, 13, 14, 15; 276 nm for compounds 8–11.

TABLE III

LUMINESCENCE OF OXYBARBITURATES AT 77 °K IN ETHANEDIOL–WATER CONTAINING 0.1 *M* SODIUM HYDROXIDE

Compound	λ_{ex} *(nm)*	λ_{em} *(nm)*	*Detection limit (μg ml^{-1})*		*Lifetime of delayed luminescence (s)*
			Total luminescence	*Delayed luminescence*	
2	260	395	0.4	0.5	3.7
5	266	395	0.3	0.5	5.6
6	266	395	0.2	0.3	6.1
7	265	410	0.3	—	—
8	265	410	0.4	—	—
9	266	410	0.2	—	—
10	266	410	0.2	—	—
11	265	410	0.1	—	—

The ethanediol–water solvent was selected because it gave reasonably clear glasses at 77 °K and had a low luminescent background. In experiments on blood extracts, it could be produced easily by addition of pure ethanediol to the aqueous extract; evaporation steps were therefore unnecessary. Under the conditions used, barbiturates with allyl and other non-aromatic unsaturated substituents (compounds 1, 4, 12–15) were only feebly luminescent, as was metharbital (compound 3). Most of the other non-N-methylated barbiturates showed a broad fluorescence band similar to that observed at room temperature, although there were small apparent blue shifts in the wavelengths of maximum excitation and emission.

The three barbiturates with 5-phenyl groups showed delayed luminescence at 77 °K ($\lambda_{em} = 395$ nm), which could be isolated and studied with the phosphoroscope. This emission band showed a considerable degree of vibrational fine structure (Fig. 1), had a lifetime of several seconds in each case, and could be used to determine submicrogram quantities of "phenobarbitones". Luminescence intensity–concentration plots were linear up to concentrations of at least 40 μg ml^{-1} of the final solution. Attempts to increase the intensity of the emission through the "heavy atom" effect, by adding small quantities of potassium bromide or potassium iodide to the solution, were not successful, though the presence of up to 5% (w/v) of the halides improved the clarity of the "glasses" formed at 77 °K.

Determinations of microgram quantities of barbiturates extracted from whole blood were successfully performed, with recoveries in the range 90–92%. Despite some increase in blank fluorescence values, detection limits frequently remained in

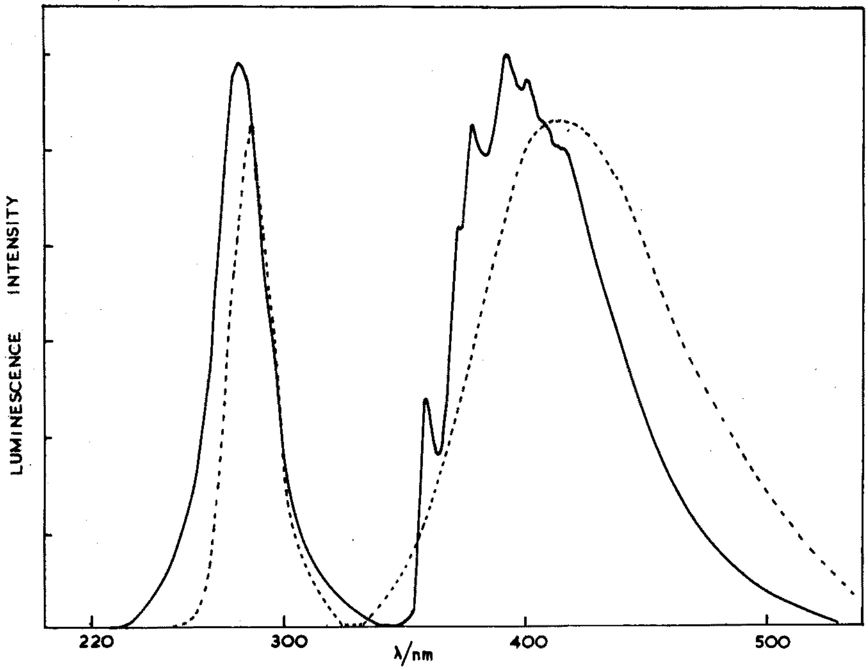


Fig. 1. Barbiturate luminescence spectra (uncorrected). The continuous line shows the excitation and delayed emission spectra of phenobarbitone (compound 6) at 77°K, and the broken line the excitation and fluorescence spectra of pentobarbitone (compound 10) at 298 °K.

the microgram range, when allowance was made for the dilutions resulting from the extraction procedures. For example, after extraction, the detection limit for barbitone (compound 7) measured at room temperature was 0.8 μg ml^{-1} in the final solvent, and the detection limit for phenobarbitone (compound 6), measured by means of the delayed luminescence at 77 °K, was 0.5 μg ml^{-1}. The standard deviation at the 5 μg ml^{-1} level in the case of barbitone was 6%.

Discussion

The results presented indicate that the scope and selectivity of the luminescence determination of oxybarbiturates are considerably enhanced if measurements can be made at 77 °K as well as at room temperature. By one or other technique, all but three of the samples studied could be determined at levels of around 1 μg ml^{-1} in the final solution. The changeover from one mode of operation of the fluorimeter to the other took only a few minutes.

Since barbiturates lacking a 5-phenyl group (compounds 1, 3, 4, 7–15) show no phosphorescence and their fluorescence intensity is not noticeably increased at 77 °K, they are best determined at room temperature. The "phenobarbitones", however, all show a delayed emission at 77 °K and it is noteworthy that the wavelength is slightly shorter than that of the prompt fluorescence of all the barbiturates. This luminescence is probably the phosphorescence of the aromatic moiety. The phosphorescence enables the "phenobarbitones" (compounds 2, 5, 6) to be determined at lower concentrations than is possible at room temperature, and allows them to be readily distinguished from other oxybarbiturates. It is particularly valuable in the case of mebaral (compound 2), which cannot be determined by room-temperature fluorescence; since the phosphorescent lifetime of this compound is different from those of phenobarbitone and rutonal (compounds 5 and 6), it seems that mebaral might be distinguished unequivocally from other oxybarbiturates by the combination of room temperature and 77 °K studies.

Various molecules which may interfere with the ultraviolet spectrophotometric analysis of oxybarbiturates *e.g.* bemegride (β-methyl-β-ethylglutarimide), which is sometimes administered in cases of barbiturate intoxication, and diphenylhydantoin, which is often given with phenobarbitone, do not interfere with the luminescence methods. Further, since the desulphurization of thiobarbiturates, and the demethylation of 1- or 3-substituted oxybarbiturates each produces profound changes in the luminescence properties of the molecules, it is likely that luminescence analyses will be of value in distinguishing such substances from their metabolic products.

Since phosphorimetry no longer involves major technical difficulties, and has a number of important advantages, it is likely that it will find increasing use in the analysis of trace quantities of drugs in biological fluids. Its value in the study of barbiturates, a weakly luminescent group of compounds, suggests that in other cases, exceedingly sensitive analyses should be feasible.

We are grateful to the companies named for generous gifts of barbiturates, and to Mr. P. Cobb of the West Midland Forensic Service Laboratory for samples of whole blood. One of us (L.A.G.) acknowledges financial assistance from the Medical Research Council.

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SHORT COMMUNICATION

The extraction–spectrophotometric determination of trace quantities of nickel in grease with dimethylglyoxime

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(Received 24th May 1972)

Dimethylglyoxime has been known as a reagent for nickel since the beginning of this century[1], and has been widely used in the gravimetric and spectrophotometric determination of the metal, as well as for its separation by extraction. Only in the last twenty years has the reagent been used for the extraction–spectrophotometric determination of nickel; the complex dissolves in benzene and isoamyl alcohol[2], but dissolves more easily in chloroform, which has been preferred by most workers.

Although the nickel dimethylglyoximate complex has two well-defined maxima at 329 and 378 nm in chloroform (Fig. 1), the former has seldom been used[2,3]. Because of the nature of the spectrum at the two maxima, and because of the large variations in the nominal maximum quoted in the literature at the longer wavelength peak[4-7], the use of the broader peak at 329 nm should be preferable to the 378-nm maximum. If the latter narrow peak is used, appreciable absorbance errors can be introduced if the procedural conditions for a particular method are not rigidly followed. Moreover, the method based on the use of 329 nm is more sensitive and obeys Beer's law better than that at 378 nm. Thus the 329-nm maximum was employed in the proposed determination of nickel in grease samples.

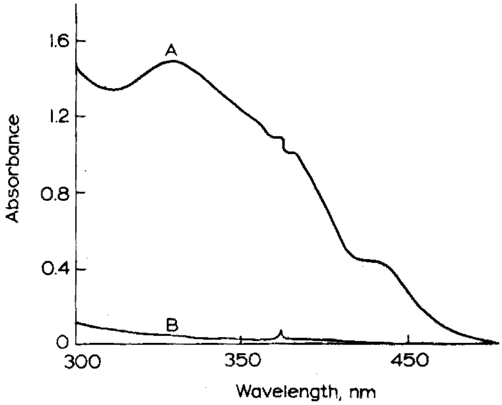

Fig. 1. Absorbance spectrum of (A) nickel dimethylglyoximate complex, 1.6 μg Ni ml^{-1}, and (B) the reagent blank in chloroform.

Experimental

Reagents. All the reagents used were of analytical grade.

Apparatus. A Unicam SP 800 u.v.–visible spectrophotometer and 1-cm fused silica cells were used.

Preparation of calibration curves. Heat aliquots of standard nickel sulphate solutions (to cover the range 0–0.8 p.p.m. in the final solution) in beakers with 1 ml of concentrated sulphuric acid (s.g. 1.84), 5 ml of concentrated nitric acid (s.g. 1.42) and 2 ml of 60% perchloric acid (s.g. 1.54) until copious sulphur trioxide fumes are evolved. Dilute the solution with water to 40 ml, add 2.5 ml of aqueous 40% (w/v) sodium citrate solution, and adjust to pH 8.8–9.4 with 3.5 *M* ammonia solution. Add 5 ml of 30% hydrogen peroxide followed immediately by 2.5 ml of a 1% (w/v) solution of dimethylglyoxime in 95% ethanol. After 15 min, extract the nickel dimethylglyoximate complex into 5.0 ml of chloroform by vigorous shaking for 1 min. To avoid turbidity in the chloroform solution, filter through a small pad of cotton wool to remove traces of water. Measure the absorbance in 1-cm cells at 329 nm against chloroform.

Preparation of sample solution. In order to avoid long wet-oxidation times and the use of large quantities of acids, the fatty material of the grease samples is first extracted into benzene. Wrap 0.1–0.2 g of sample in a small filter paper and insert it into a small Soxhlet extraction thimble. Extract until the benzene appears colourless in the Soxhlet. Remove the residual material in the folded paper from the thimble and evaporate the residual benzene immediately. Oxidize with the mixed acids as described above. Dilute the resulting sulphuric acid solution with water and filter through a small sintered glass funnel to remove any silica present. Divide the filtrate (50 ml) into duplicate aliquots and treat them as described above for the standard solutions. Prepare a blank solution similarly.

Results and discussion

Absorbance spectrum. The absorbance spectrum of the nickel dimethylglyoximate complex in chloroform is shown in Fig. 1. The molar absorptivities at 329 and 378 nm are $5.1 \cdot 10^4$ and $3.6 \cdot 10^4$, respectively. It is clear that the use of the broad peak at 329 nm would introduce fewer errors in routine work.

Standard curves, precision and accuracy. The standard curves for the nickel range 0–0.8 μg ml^{-1} in the absorbing solution are shown in Fig. 2. As can be seen from the curves, the 329-nm maximum gives a standard curve which obeys Beer's law better than that at 378 nm. Thus the use of 329-nm maximum should give more accurate results. Ten replicate nickel determinations in the sample aliquots (with an average equivalent to 0.69 μg Ni in the aliquots) at the 329-nm maximum gave a coefficient of variation of 8.7%. This shows that the precision of the method based on the 329-nm maximum is good. Results of a recovery test for standard nickel solutions added to grease samples before wet oxidation (Table I) indicate good accuracy as well.

The use of hydrogen peroxide in the method. The samples used in this work contained appreciable quantities of iron. Since iron(II) forms a complex with dimethylglyoxime, it was oxidized to iron(III) which does not react[8]. Hydrogen peroxide was chosen as the oxidant; 5 ml of 30% hydrogen peroxide was used in 50 ml of the aqueous solution. It was advisable to leave the solution after the peroxide addition for at least 15 min before extraction of the complex, since the red coloration takes

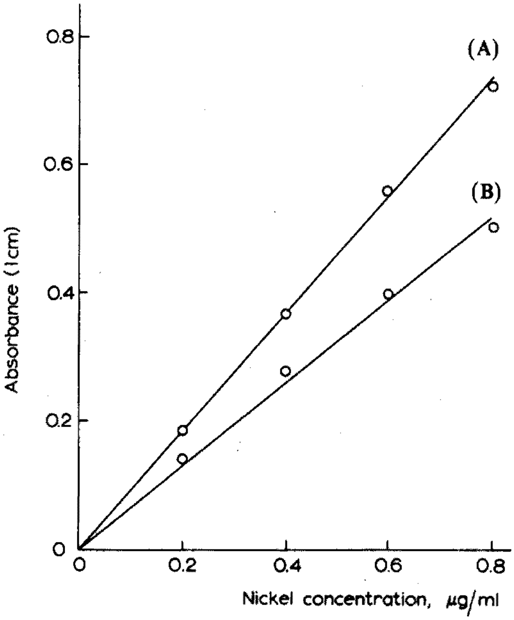

Fig. 2. Standard curves for nickel determination with dimethylglyoxime in chloroform: (A) at 329 nm and (B) at 378 nm.

TABLE I

ACCURACY TEST

Ni added (µg)	Nil	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
Total Ni found (µg)	0.65	1.63	2.60	3.63	4.60	5.63	6.68	7.50	8.43	9.35
% Recovery	—	98	97	99	99	100	101	98	97	97

longer to appear in the presence of hydrogen peroxide than in its absence. The hydrogen peroxide did not interfere with the method at this concentration suggested.

I am grateful to Mr. C. L. Tarimu, Director of the East African Industrial Research Organization, for reading through the manuscript and for permission to publish this work.

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SHORT COMMUNICATION

Extraction-spectrophotometric determination of osmium with bismuthiol-II in presence of most of the platinum metals and other ions

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(Received 16th May 1972)

Several organic reagents containing mercapto groups attached to heterocyclic rings have been utilized for the spectrophotometric determination of osmium[1,2] but these reagents yield coloured products of low stability. In order to improve on the rather limited success of these reagents, two reagents of similar nature, 2,5-dimercapto-1,3,4-thiodiazole (bismuthiol-I) and phenyldithiobiazolonethiol (bismuthiol-II) have been examined. Bismuthiol-I forms an unstable green colour with osmium(VIII), but bismuthiol-II, previously used as a reagent for some of the platinum metals[3,4], yields a green precipitate with osmium(VIII) which may be extracted with ethyl or amyl acetate or amyl alcohol. The ethyl acetate extract on dilution with ethanol remains stable for a considerable time and so is suitable for the spectrophotometric determination of osmium. The coloured complex obeys Beer's law over a useful range and has been successfully utilized to separate and determine small amounts of the element from a large number of other ions including the platinum metals (except palladium).

Experimental

Apparatus and reagents. A Hilger Uvispek spectrophotometer with 1-cm glass cells was used.

A standard solution of osmium was prepared from the tetroxide[5]. The solution was also standardized iodimetrically[6].

Standard solutions of diverse ions were prepared from their chloride, nitrate, ammonium or sodium salts; the solutions were standardized by conventional methods.

The reagent was prepared by the method of Busch[7]; a 1% (w/v) solution in ethanol was used.

Buffer solutions used were prepared by conventional procedures. All other reagents were of the highest chemical purity.

Absorbance curve. A known amount of osmium solution was treated with 5 ml of water and 5 ml of sodium acetate–hydrochloric acid buffer solution of pH 3.0. Then 2.5 ml of reagent solution were added and the mixture was extracted with 5 ml of ethyl acetate. After separation of the layers, the extract was transferred to a 25-ml calibrated flask. The 50-ml separatory funnel was washed twice with 5-ml portions of ethanol and the washings were combined with the extract, which was made up to

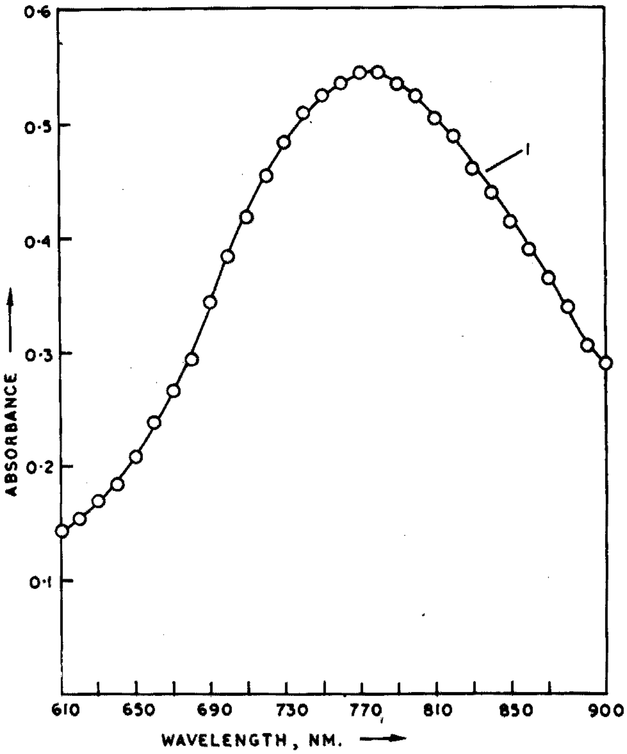

Fig. 1. Absorption curve, 9 p.p.m. osmium.

volume with ethanol. The absorbance of the solution was measured against a reagent blank prepared in the same way. The absorbance curve (Fig. 1) shows a maximum at 770–780 nm. As the reagent showed no absorption above 700 nm, measurements were made with ethanol as the blank solution.

Acidity and reagent. The complex showed constant colour intensity from 1 *M* hydrochloric acid to pH 4.5. The acidity was adjusted with 6 *M* hydrochloric acid, pH values up to 4.5 with sodium acetate–hydrochloric acid buffer, and pH values over 4.5 with sodium acetate–acetic acid buffer. A volume of 2.0 ml of the reagent solution sufficed to produce full colour intensity up to 15 p.p.m. of osmium. Addition of more reagent, however, had no effect.

Beer's law, optimal range, sensitivity and photometric error

The colour system was found to obey Beer's law from 3 to 15 p.p.m. of osmium. A Ringbom plot[8] showed that the optimal range was 3.0–10.5 p.p.m. The percent relative error[9] in this range was 2.72.

The Sandell sensitivity[10] was found to be 0.0163 μg Os cm^{-2} and the molar absorptivity was calculated to be 11,700.

Composition of the complex

The composition of the complex in solution was ascertained by Job's method of continued variation[11] and by the molar ratio method[12].

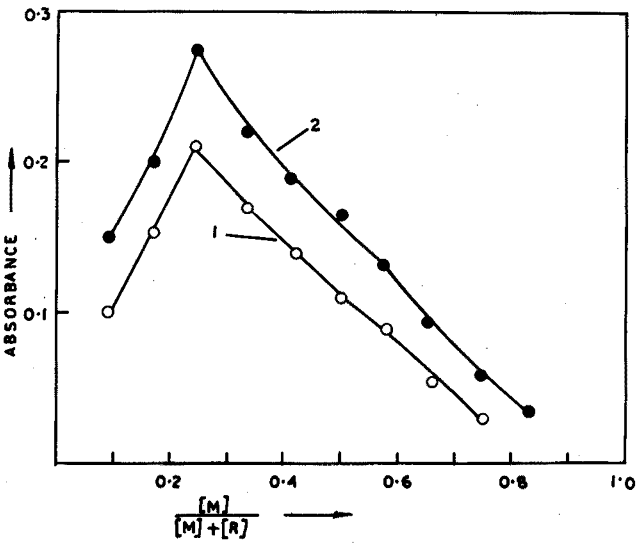

Fig. 2. Composition by Job's method. (1) Os(VIII) = reagent = $5.0 \cdot 10^{-4}$ M; (2) Os(VIII) = reagent = $7.5 \cdot 10^{-4}$ M.

For Job's method, the colour of the complementary mixtures (12 ml total volume) of equimolar solutions of the metal and the reagent was developed and extracted in presence of 10 ml of sodium acetate–hydrochloric acid buffer solution of pH 3.0, as described for the absorption curve. The absorbance was measured at 780 nm. The maximum (Fig. 2) indicates the formation of a 1:3 complex.

For the molar ratio method, equimolar solutions ($1 \cdot 10^{-3}$ M) of the metal and the reagent were mixed in ratios varying from 1:0.5 to 1:5.0 and the absorbance of the colour after development, as described for the absorption curve, was measured at 780 nm. The curve obtained confirmed the formation of a 1:3 complex.

To evaluate the dissociation constant of the complex, mixtures of non-equimolar solutions of the metal and the reagent were prepared as described for Job's method and their absorbances were measured at 780 nm. From the data obtained (Fig. 3), the dissociation constant, K, was calculated as reported earlier[13]. The results are given in Table I.

The degree of dissociation, α, and the dissociation constant, K, were also calculated from the equation of Harvey and Manning[14]. The value of α was found to be 0.298 and that of the dissociation constant, K, $3 \cdot 10^{-10}$.

TABLE I

CALCULATION OF DISSOCIATION CONSTANT

Osmium concn.	*Reagent concn.*	*m*	*n*	*X*	*p*	*K*
$5.0 \cdot 10^{-4}$ M	$2.0 \cdot 10^{-3}$ M	1	3	0.56	4	$1.3 \cdot 10^{-10}$
$4.5 \cdot 10^{-4}$ M	$1.8 \cdot 10^{-3}$ M	1	3	0.56	4	$1.1 \cdot 10^{-10}$

Mean $K = 1.2 \cdot 10^{-10}$

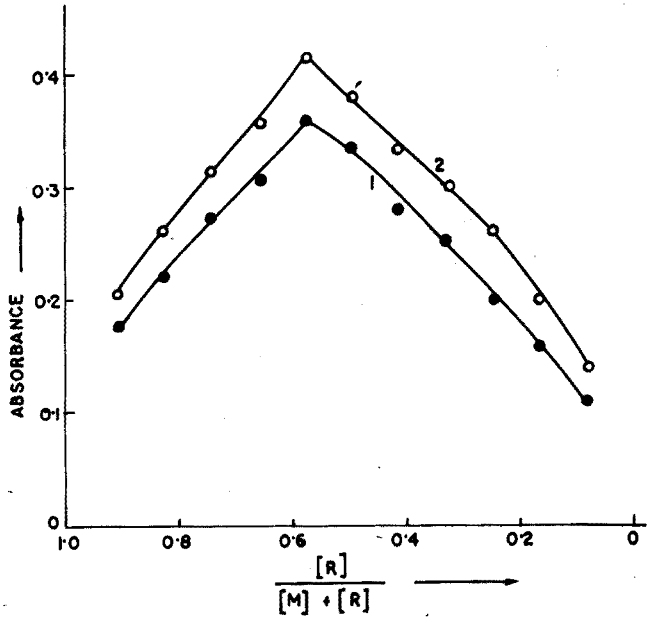

Fig. 3. Job's method of dissociation constant. (1) Os(VIII) = $4.5 \cdot 10^{-4}$ *M*, reagent = $1.8 \cdot 10^{-3}$ *M*; (2) Os(VIII) = $5.0 \cdot 10^{-4}$ *M*, reagent = $2.0 \cdot 10^{-3}$ *M*.

Separation from other ions

By the procedure described, as little as 6 p.p.m. of osmium could be separated and determined from the following ions (p.p.m. in parentheses): Ir^{4+}(100), Pt^{4+}(100), Ru^{3+}(100), Rh^{3+}(100), Ni^{2+}(400), Co^{2+}(400), Fe^{3+}(400), Cr^{3+}(400), Mn^{2+}(400), Zn^{2+}(400), Ti^{4+}(400), Zr^{4+}(400), V^{5+}(400), Mo^{6+}(400), W^{6+}(400), UO_2^{2+}(400), As^{5+}(400), La^{3+}(400), Mg^{2+}(400), Sr^{2+}(400), Ba^{2+}(400), Al^{3+}(400), Ca^{2+}(400), Th^{4+}(400), rare earths (400), citrate (400), oxalate (400), tartrate (400), phosphate (400), EDTA (400) and fluoride (400). However, Cu^{2+}, Cd^{2+}, Pb^{2+}, Tl^{+}, Ag^{+}, Pd^{2+}, Sb^{3+} and Bi^{3+} interfered.

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SHORT COMMUNICATION

Extraction de l'acide nitrique et des lanthanides par l'hexabutylphosphorotriamide

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(Reçu le 10 juin 1972)

Un nombre considérable de travaux a déjà été publié sur l'extraction liquide–liquide des lanthanides et des actinides par les composés organophosphorés neutres. Parmi ceux-ci, les esters phosphoriques occupent une place importante. Plus récemment, des composés tels que les oxydes de phosphine ont été étudiés et se sont révélés être d'excellents agents d'extraction en raison de la "basicité" de leur groupement phosphoryle PO[1–3]. Dans ce travail, nous nous sommes intéressés à des phosphoramides.

L'hexaméthylphosphorotriamide (HMPT) est connu depuis longtemps pour ses propriétés en tant que solvant et milieu réactionnel en chimie organique[4,5]. Nous avons montré antérieurement[6,7] son comportement d'agent extractant à partir de nitrates alcalins fondus qui a permis de réaliser une séparation totale des lanthanides lourds et légers (et même des lourds-moyens dans certaines conditions). Il nous a semblé intéressant d'étudier un tel type d'agent en extraction liquide–liquide à 25°. Toutefois, pour simplifier cette étude, nous avons utilisé un dérivé rendu insoluble dans l'eau en remplaçant les groupements méthyles par des groupements alcoyles plus lourds. Ayant trouvé[8] que l'hexabutylphosphorotriamide (HBPT) possède les mêmes propriétés extractantes que l'HMPT à partir de nitrates alcalins fondus, nous l'avons choisi comme agent d'extraction d'éléments de terres rares à partir de solutions aqueuses.

Dans ce but, l'étude préliminaire de l'extraction de l'eau et de l'acide nitrique par l'HBPT est nécessaire pour l'interprétation de la distribution des lanthanides entre les phases aqueuse et organique.

Partie expérimentale

Produits utilisés. L'hexabutylphosphorotriamide [$(Bu_2N)_3PO$] a été synthétisé[9] par action de la di-n-butylamine sur le trichlorure de phosphore, puis oxydation du produit obtenu par l'eau oxygénée.

Les radioisotopes des lanthanides employés sont obtenus par irradiation des oxydes correspondants dans la pile Mélusine du C.E.N.G. de Grenoble. Les autres réactifs utilisés sont des produits R.P. pour analyses.

Mode opératoire. Les extractions sont réalisées à 25° ±0.5° dans un système identique à celui décrit antérieurement[10]. Les tubes SOVIREL utilisés ont un volume de 45 cm^3 et contiennent deux phases constituées par 10 cm^3 de phase organique (toluène) dans laquelle l'HBPT est mis en solution, et 10 cm^3 de phase aqueuse dont la force ionique est maintenue constante avec une solution de nitrate sodique 2 *M*; le pH est fixé à l'aide de l'acide nitrique. Les métaux sont introduits sous forme de nitrates.

Les mesures de partage sont effectuées sur les phases aqueuse et organique séparées après une durée d'agitation de 3 h, suffisante pour atteindre l'équilibre.

Dosages. L'acide nitrique a été titré potentiométriquement par la soude, dans l'eau pour les phases aqueuses, dans l'éthanol pour les phases organiques[1] après addition de 5 cm^3 de phase organique dans 25 cm^3 d'éthanol (en ayant soin de reconditionner l'électrode en verre entre chaque dosage).

L'eau a été dosée par la méthode de Karl Fischer avec une cellule identique à celle préconisée par Bizot[11]. Le montage de détection coulométrique utilisé était soit un chronoampérostat Tacussel type CEAMD plus un Titravit Prolabo, soit un montage coulométrique simple.

L'HBPT en solution organique a été titré potentiométriquement[12] par une solution d'acide perchlorique dans l'acide acétique.

Les coefficients de partage des lanthanides ont été déterminés en mesurant l'activité des phases aqueuse et organique par spectrométrie-γ à l'aide d'un Didac 800 canaux Intertechnique équipé d'une sonde NaI dopé au thallium. Les comptages ont été effectués sur des volumes de phase identiques dans des béchers de même calibre.

Distribution de l'eau et de l'acide nitrique entre une phase aqueuse et une phase organique de HBPT (toluène)

La teneur en eau de saturation du toluène a été vérifiée en équilibrant des volumes égaux de toluène et d'eau. La concentration de saturation est de 0.020 mol l^{-1}, valeur en accord avec celles trouvées précédemment dans la littérature[13,14].

De même, le partage simple de l'acide nitrique entre le toluène et l'eau n'est notable qu'à partir de solutions d'acide nitrique de concentrations supérieures à 5 *M*.

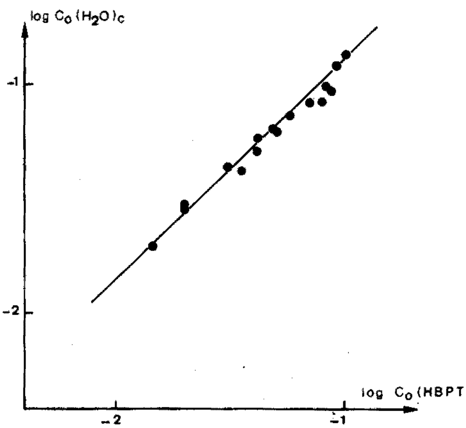

Fig. 1. Hydratation de l'HBPT en solution dans le toluène.

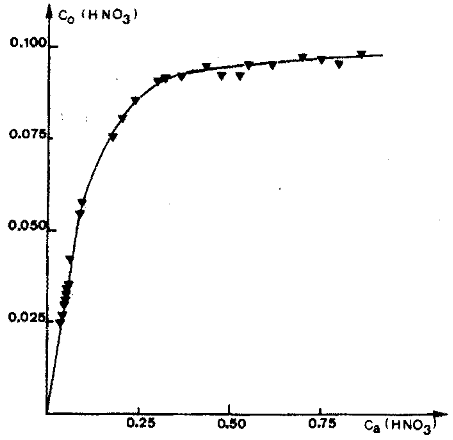

Fig. 2. Partage de l'acide nitrique entre une phase aqueuse (2 *M* $NaNO_3$) et une solution 0.1 *M* de HBPT dans le toluène.

Distribution de l'eau. L'hydratation de l'HBPT en solution dans le toluène est représentée sur la Fig. 1. En ordonnées, $C_0(H_2O)_c$ représente la concentration totale en eau en phase organique moins la concentration de saturation en eau du toluène, et C_0(HBPT) la concentration en HBPT libre. La courbe obtenue est une droite de pente 1 pour les concentrations en HBPT jusqu'à 0.1 *M*. Les équilibres sont obtenus par agitation d'une solution de nitrate sodique 2 *M* avec une phase organique de composition variable en HBPT.

Distribution de l'acide nitrique. La Fig. 2 illustre les résultats concernant la distribution de l'acide nitrique entre une phase aqueuse 2 *M* en nitrate sodique, de concentration variable en acide nitrique et une phase organique 0.1 *M* en HBPT. Cette courbe est analogue à celle obtenue dans le cas de l'oxyde de tributylphosphine[15] dans les mêmes conditions de concentrations.

Discussion des résultats

Cas de l'eau. L'hydratation de l'HBPT peut être attribuée à un équilibre du type:

$$\mathrm{HBPT}_0+\mathrm{H_2O_a}\rightleftarrows(\mathrm{HBPT,\ H_2O})_0 \qquad (1)$$

En supposant que, dans ces conditions, l'activité de l'eau en phase aqueuse ne varie pas et que le rapport des coefficients d'activité des espèces en phase organique est constant, à cet équilibre correspond:

$$K'_{\mathrm{H_2O}} = [\mathrm{HBPT,H_2O}]_0/[\mathrm{HBPT}]_0$$

Pour des concentrations en HBPT < 0.1 *M*, la Fig. 1 montre que l'hydratation de l'HBPT dans le toluène est bien régie par l'équilibre (1). Il se forme l'espèce HBPT, H_2O.

Dans les mêmes conditions de concentrations, des résultats analogues avaient été obtenus pour différents agents d'extraction: tributylphosphate[16], oxyde de tri-n-butylphosphine[15,17].

La constante $K'_{\mathrm{H_2O}}$ peut être calculée à partir de la Fig. 1: $K'_{\mathrm{H_2O}}=0.92\pm0.1$.

Cas de l'acide nitrique. Nous pouvons supposer qu'en phase organique il y a neutralisation entre l'agent extractant à caractère basique et l'acide nitrique avec formation d'un complexe 1:1 suivant l'équilibre:

$$\mathrm{H^+_a}+\mathrm{NO^-_{3a}}+\mathrm{HBPT}\rightleftarrows(\mathrm{HBPT,\ HNO_3})_0 \qquad (2)$$

En admettant comme précédemment que le rapport des coefficients d'activité des espèces en phase organique est constant et en se rappelant que nous travaillons en milieu nitrate sodique 2 *M*, nous pouvons écrire, en désignant par $C_a(HNO_3)$ la concentration en acide nitrique en phase aqueuse, que la constante apparente est:

$$K'_1=[\mathrm{HBPT,HNO_3}]_0/C_a(\mathrm{HNO_3})[\mathrm{HBPT}]_0$$

Dans le domaine de concentration exploré, la concentration en acide nitrique passant dans le toluène seul est négligeable, donc $[\mathrm{HBPT,HNO_3}]_0$ peut être assimilée à la concentration $C_0(HNO_3)$ en acide nitrique en phase organique à l'équilibre tandis que $[\mathrm{HBPT}]_0$ (concentration en agent extractant libre) peut être obtenue par différence entre la concentration totale en HBPT en phase organique et $C_0(HNO_3)$.

Si l'hypothèse d'un complexe extrait de la forme (HBPT, HNO_3) est vérifiée, la courbe

$$\log [\text{HBPT}, \text{HNO}_3]_0/[\text{HBPT}]_0 = \text{f}(\log C_a(\text{HNO}_3))$$

doit être une droite de pente 1. Nous voyons (Fig. 3) que, dans les conditions présentes, nos résultats permettent de conclure à l'extraction d'un seul complexe HBPT, HNO_3 et de dire que la constante apparente d'équilibre d'extraction de HNO_3 par HBPT a pour valeur: $K'_1 = 12.7 \pm 2$ $(\text{mol/l})^{-1}$.

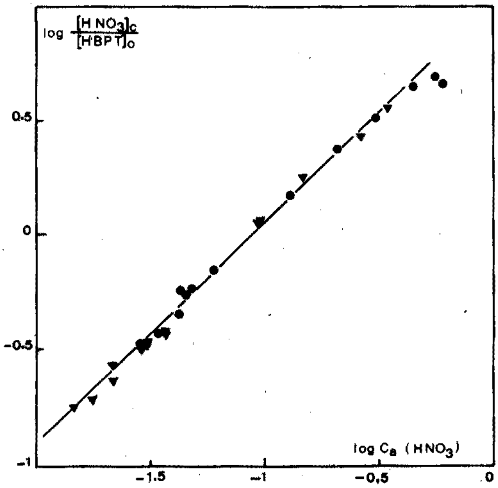

Fig. 3. Détermination graphique de la stoechiométrie du complexe HBPT, HNO_3. (●) Solution HBPT 0.100 *M* dans le toluène, (▼) solution HBPT 0.150 *M*.

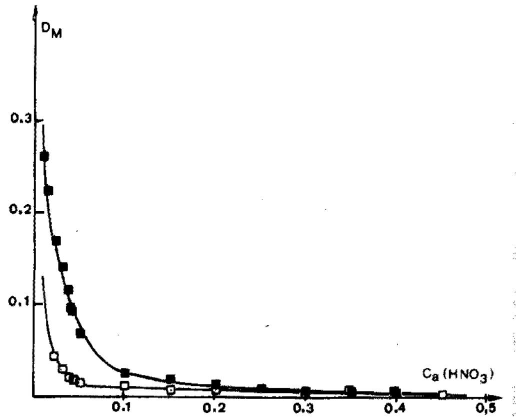

Fig. 4. Influence de la concentration en acide nitrique en phase aqueuse sur le coefficient de partage des lanthanides. Force ionique de la phase aqueuse 2 *M* $NaNO_3$. C_0 (HBPT) initiale = 0.100 *M*. □ Tb, ■ Tm.

Extraction des lanthanides par l'HBPT

La distribution du terbium et du thulium avec une solution de HBPT 0.1 *M* dans le toluène a été déterminée en fonction de la concentration en acide nitrique (Fig. 4); elle a permis d'examiner l'influence de cet acide.

D'autre part, nous avons déterminé la stoechiométrie des complexes lanthanides–HBPT extraits en étudiant les distributions de l'europium, du thulium et de l'ytterbium, à force ionique constante 2 *M* en nitrate de sodium et avec une concentration en acide nitrique en phase aqueuse fixée à 10^{-2} *M*.

En supposant l'équilibre de distribution suivant:

$$3\text{NO}_{3\text{a}}^- + \text{M}_\text{a}^{3+} + n\ \text{HBPT} \rightleftarrows \text{M(NO}_3)_3, n\ \text{HBPT}$$

avec la constante apparente d'équilibre correspondante:

$$K'_\text{M} = [\text{M(NO}_3)_3, n\ \text{HBPT}]_0/[\text{M}^{3+}]_\text{a}\ [\text{HBPT}]_0^n \qquad (3)$$

le rapport $[\text{M(NO}_3)_3, n\,\text{HBPT}]_0/[\text{M}^{3+}]_\text{a}$ représente le coefficient de partage du métal $D_\text{M} = [\text{M}^{3+}]_0/[\text{M}^{3+}]_\text{a}$.

En passant à la valeur logarithmique de l'expression (3), on obtient: $K'_M = D_M/[HBPT]_0^n$ et log $D_M = n$ log $[HBPT]_0 + \log K'_M$; $[HBPT]_0$ représentant la concentration en HBPT libre en phase organique. Cette concentration se déduit aisément de $[HBPT]_{totale} = [HBPT]_T$ connaissant K'_{H_2O}, $K'_{HNO_3} = K'_1$ et $C_a(HNO_3)\cdot$ $[HBPT]_0 = [HBPT]_T/C_0 + K'_{H_2O} + K'_1 C_a(HNO_3)$.

Si nous traçons les courbes log $D = f(\log[HBPT]_0)$, celles-ci doivent être des droites dans le cas où un seul complexe est extrait. La pente et l'ordonnée à l'origine de ces droites donnent respectivement la valeur de n et de K'_M. La Fig. 5 montre que les complexes des lanthanides avec l'HBPT sont de la forme $M(NO_3)_3$, 2 HBPT. Les constantes apparentes d'équilibre d'extraction sont: $K'_{Eu} = 123 \pm 15$ (mol/l)$^{-2}$; $K'_{Tm} = 257 \pm 26$ (mol/l)$^{-2}$; $K'_{Yb} = 257 \pm 26$ (mol/l)$^{-2}$.

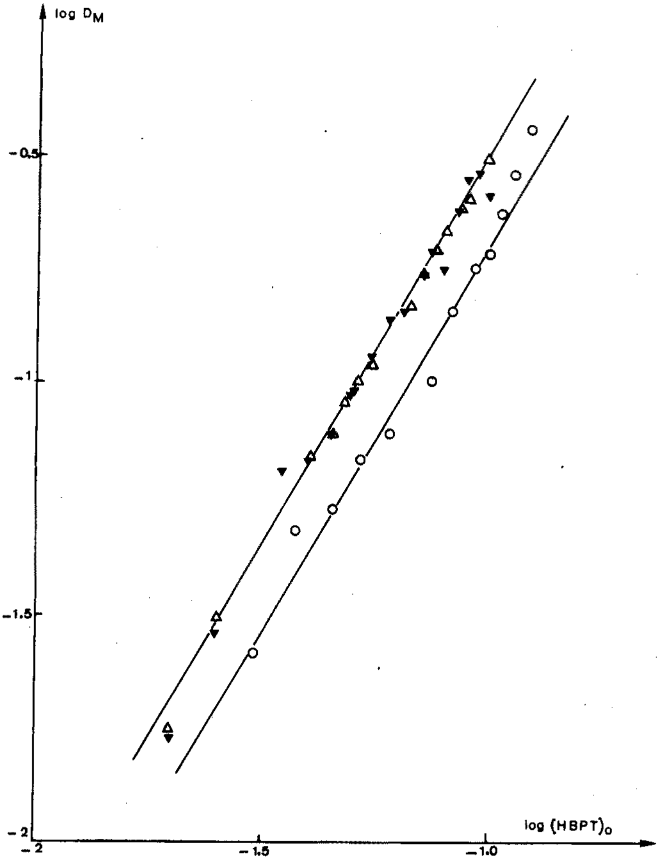

Fig. 5. Détermination graphique de la structure des complexes $M(NO_3)_3$, 2 HBPT. Force ionique de la phase aqueuse 2 *M* en $NaNO_3$. M = Eu ○, Tm ▼, Yb △.

Ainsi les complexes extraits à 25° par l'HBPT ont la même forme que ceux[6] extraits à partir de nitrates fondus à 160°. Les résultats montrent que les valeurs des constantes apparentes d'équilibre d'extraction, dans la série des lanthanides, augmentent avec le numéro atomique, comme dans le cas de la distribution à partir de milieu fondu[8]. Ainsi des séparations de lanthanides lourds, lanthanides légers sont possibles.

Cependant, dans les conditions de la présente étude, les valeurs de ces constantes restent bien inférieures à ce que nous obtenons à partir des nitrates fondus.

Comparativement aux résultats obtenus par Goffart et Duyckaerts dans le cas de la TOPO[3], les coefficients de partage obtenus pour les lanthanides avec notre agent sont sensiblement identiques mais les formes des complexes extraits sont différentes de ($M(NO_3)_3$, 3 TOPO), vraisemblablement pour des questions d'encombrement stérique.

D'autre part, une différence importante réside dans le comportement de l'HBPT en fonction de l'acidité. En effet, nous n'observons aucune valeur maximale de D_M. Dans notre cas, D_M diminue lorsque la concentration en HNO_3 augmente ce qui signifie que la formation de HBPT, HNO_3 interfère notablement. Il en résulte une forte diminution de valeur de D_M. Lorsque HBPT est totalement sous forme associée avec l'acide nitrique, D_M atteint alors une valeur limite.

Néanmoins la présence d'une certaine quantité d'acide nitrique dans le système nous est apparue nécessaire pour éviter des phénomènes de précipitation. Dans le cas présent une concentration de HNO_3 10^{-2} M est suffisante et a un effet inhibiteur négligeable.

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ANNOUNCEMENTS

24th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy

The 24th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Cleveland Convention Center, Cleveland, Ohio, U.S.A., March 5–9, 1973. An estimated 350 papers on all phases of Analytical Chemistry and Spectroscopy will be presented. Symposia on the following subjects are now being arranged.

Liquid Chromatography—Analytical Bridge to Spectroscopy.
Three-Dimensional Microcompositional Analysis—The Advent of Ion-Probe Mass Spectrometry.
Industrial Applications of ^{13}C N.M.R.
Forensic Science.
Women in Mass Spectrometry.
Industrial Research—Is It Worth It?
Guidelines for Defining and Implementing the Computerized Laboratory System (ASTM).
The Analysis of Slags and Related Oxide-type Materials (ASTM).
Coblentz Society Award Symposium.
Spectroscopy Society of Pittsburgh Award Symposium.

Papers are *not* restricted to the symposium topics and original papers on all phases of Analytical Chemistry and Spectroscopy are invited.

Authors wishing to present papers at the 1973 Pittsburgh Conference should submit three copies of a 150 word abstract to: H. L. Retcofsky, Program Chairman, 1973 Pittsburgh Conference, U. S. Bureau of Mines, 4800 Forbes Avenue, Pittsburgh, Pa. 15213, U.S.A. Abstract forms are available from the Program Chairman. The names and complete addresses of all authors should be included with all abstracts submitted and the name of the person who will present the paper should be underlined. The final data for receipt of abstracts is October 1, 1972.

In addition to the program of technical papers, more than 250 companies, both foreign and domestic, will be represented at the exposition of Modern Laboratory Equipment, the largest exposition of analytical instrumentation and related materials in the world. Information concerning the exhibits should be directed to: Robert E. Witkowski, Exposition Chairman, 1973 Pittsburgh Conference, Westinghouse Electric Corporation, Research Laboratories, Churchill Boro., Pittsburgh, Pa. 15235, U.S.A.

Second Australian Symposium on Analytical Chemistry

Kensington, May 14–18th, 1973

The analytical chemistry division of the Royal Australian Chemical Institute will be holding its second symposium on analytical chemistry at the University of New South Wales, Kensington, on May 14–18th, 1973. Papers dealing with all aspects of analytical chemistry including biochemical, clinical, mineral, metallurgical, environmental, modern instrumental, pharmaceutical, educational, and data handling and processing will be accepted. Further information may be obtained from the Hon. secretary: Mr. L. S. Dale, Australian Atomic Energy Commission, Research Establishment, Private mail bag, P.O. Sutherland, N.S.W. 2232, Australia.

International Symposium on Microchemical Techniques—1973

Progress and Projections for Microchemistry will be the general theme for the International Symposium on Microchemical Techniques—1973. The symposium will be held at The Pennsylvania State University, University Park, Pennsylvania, August 19–24, 1973 and will be conducted by the American Microchemical Society, with the sponsorship of the International Union of Pure and Applied Chemistry.

The scientific program will consist of sessions dedicated to topics of current interest, general papers, discussion groups, practical demonstrations, an equipment exhibit, and will also include a number of instructional workshop sessions. Special sessions will be included on such topics as:

Automated Elemental Analyzers—Ten Years Later.
Computers in Elemental Analysis.
Organic Elemental Analysis—New Methods and Equipment.
Environmental Microanalysis—New Sensors and Techniques.
Microelectrodes.
Forensic Analysis—Narcotics and Drugs of Abuse.
Organic Functional Group Analysis—New Directions.
Electroanalytical Advances, including Ion Selective Electrodes.
Microscale Separations—Advances in Techniques and Methods.
Standards and Standardization for Microchemistry and Microanalysis.
Trace Analysis—Advances in Organic and Inorganic Analysis.
New Techniques in Microchemistry.

Persons interested in presenting a paper under any of the above topics, or a paper on the general topic of microchemistry, should submit their paper to: Mr. Howard J. Francis, Jr., Pennwalt Corporation, 900 First Avenue, King of Prussia, Pa. 19406, U.S.A. Included in the program of scientific presentations will be classroom workshops on the topics of Applications of Ion Selective Electrodes; and Theory and Applications of Thermal Methods of Analysis.

A number of semi-technical and social events are planned, an introductory evening mixer, a banquet, a social evening, an evening demonstration of gadgets, and an evening session on "The Art of Presenting a Paper." Ladies and families are welcome to attend. A separate program is planned for the ladies as well as for the children. Utilizing the excellent facilities of The Pennsylvania State University for both the technical program and housing, expenses will be minimal. A later announcement will be made concerning the program details.

5th European "Food" Symposium

The 5th European Symposium on *Food—Rheology in Food Processing and Food Quality* will take place from October 10–15, 1973, in Zürich. The symposium will be divided into the following groups of themes:

Rheological properties

Implications of rheological properties in general food processing.

Implications of rheological properties in processing of the following commodities: milk and cheese; cereals and starches; fruits and vegetables; confectionery including chocolate; meat, fish and eggs; oils and fats.

Rheological properties, food quality and consumer acceptance.

Persons interested to receive the first circular in autumn 1972 are asked to write to the secretariat, c/o Dr. W. Fritsche, Gesellschaft Deutscher Chemiker, D-6000 Frankfurt (M), Postfach 119075, G.F.R.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam – Printed in The Netherlands

BOOK REVIEWS

Annual Reports on NMR Spectroscopy, Vol. 4, Edited by E. F. Mooney, Academic Press, London, 1971, xiii + 548 pp., price £10.00.

The fourth volume in this series contains six independent contributions, two of which are annual reviews of proton and fluorine n.m.r. spectroscopy and the remainder are subject reviews of a more specialist nature.

In the first chapter G. R. Bedford surveys proton n.m.r. spectroscopy for 1969. On account of the large amount of published work in this area the reviewer has wisely selected a few important areas, including experimental techniques and biological studies, for particular attention. It is somewhat unfortunate that the material in one of the selected topics (conformational analysis) overlaps considerably with the next chapter which deals with the use of n.m.r. spectroscopy to investigate conformational change. The latter review by I. O. Sutherland is concerned with the rates of rotation around single and double bonds in organic compounds, and with inversion of alicyclic rings and trivalent pyramidal molecules. These are areas of considerable current interest and have been recently reviewed elsewhere; however, the present review is probably the most comprehensive and it also summarises very adequately the classical and density matrix theories of site exchange. Conformational changes in organometallic compounds are not discussed but it is doubtful if this chapter could have been expanded any further as it is the largest in the book. This is an authoritative and well written critical review of an area where the author has himself made many notable contributions to the original literature.

Chapter 3 by R. Haque and D. R. Buhler, reviews the applications of n.m.r. spectroscopy in the area of pesticide chemistry. The review is mainly concerned with proton spectra, but there are occasional references to spectra of other nuclei (particularly ^{31}P). The coverage appears to be quite comprehensive, including organophosphates, carbamates, phenols, hydrazides, nitriles, pyridinium compounds, and chlorinated alicyclics. This chapter also includes sections on the photochemistry and metabolism of pesticides, and discusses the applications of n.m.r. spectroscopy to investigate interactions between pesticides and proteins or clay surfaces. The fourth chapter by C. W. Haight is intended as a guide to the use of iterative computer methods in the analysis of high resolution n.m.r. spectra. It is a step-by-step account of how to proceed, including details of computer input, and the author has deliberately avoided detailed discussion of the programme structure or the underlying theory. The text is illustrated with sections of line-printer output from the author's very efficient programmes LAME and LACX (based on the Castellano and Bothner-By approach), though the alternative method of Swalen and Reilly is briefly discussed. This well written chapter is very timely and will have a wide appeal to the non-specialist as computer-assisted analysis is rapidly becoming a routine technique.

The next chapter by M. E. A. Cudby and H. A. Willis reviews the n.m.r. spectra of polymers; experimental aspects and the spectra of common synthetic polymers and copolymers are discussed. This review is very brief (*ca.* 25 pages) and does not do justice to the rather general title, as it is mainly concerned with the analysis of polymer spectra. Thus the spectra are discussed in terms of three parameters, namely chemical shift, coupling constant, and band area; the fourth parameter, relaxation time, is not discussed even though it is of great importance in n.m.r. studies of polymers. The final chapter consists of an annual review of ^{19}F spectroscopy for 1969 by K. Jones and E. F. Mooney. This chapter is a very comprehensive compilation of literature data and is to be a regular feature of the series. However, the growth of interest in this area is so great that this section is in danger of imbalancing the series, though the large amount of tabulated data could have been considerably condensed. One could also make a case for an annual review of ^{13}C or ^{31}P n.m.r. spectroscopy though this would be at the expense of the highly desirable specialist reviews.

This is an excellent and highly desirable series which covers very diverse areas of n.m.r. spectroscopy. Volume four maintains the customary high standard of contributions, and considering that it contains *ca.* 550 pages it must be regarded as reasonable value in these days of extortionate book prices.

W. B. Jennings (Birmingham)

A. K. Majumdar, *N-Benzoylphenylhydroxylamine and its analogues*, (International series of monographs in analytical chemistry, Vol. 50) Pergamon Press, Oxford, 1972, x + 210 pp., price £7.00.

Over the last two decades there has been an abundance of papers dealing with the analytical uses of N-benzoylphenylhydroxylamine (BPHA) and its various analogues. The individual papers have appeared in many languages and in journals of varied ease of access, and thus it is perhaps timely that a monograph should appear, collecting and arranging the information from these papers and organising the whole into a reasonably sized volume.

The analytical functional group of these phenylhydroxylamines is an inselective chelate system; for example 23 metals may be determined gravimetrically with BPHA. Thus selectivity must be imposed by masking, pH control and similar devices. However, since the metal complexes are relatively highly stable, they can generally be quantitatively separated from others. By suitable tailoring of the ancillary parts of the molecules it is possible to devise reagents suitable for gravimetric or spectrophotometric determinations. The author generally indicates for most of the methods quoted, what are the metals which may interfere in the determination of the analyte.

As has come to be expected from this series of monographs, of which this is the fiftieth volume, the work is well presented and arranged by a practising analyst so that other workers can obtain the optimal benefit from it.

L. S. Bark, Salford

Marvin C. Tobin, *Laser Raman Spectroscopy*, Wiley–Interscience, New York, 1971, xi + 171 pp., price £6.50.

This volume comprises Volume 35 of the series *Chemical Analysis* and contains four chapters: The Nature of the Raman Effect, Experimental Methods, The Interpretation of Raman Spectra, and Some Recent Applications together with a comprehensive bibliography covering the period 1968–1969.

Theory is presented in sufficient detail to facilitate the interpretation of spectra and as a basis for the study of more advanced texts. Spectrometer optical arrangements and components are explained in detail, sample handling described and signal to noise theory introduced for optimisation of results. The concept of group frequencies is introduced in interpretation of spectra and extensive tabulations of experimental data provided. The author points out that most published work deals with elucidation of molecular structure or studies in crystal physics and draws attention to the field of quantitative analysis and the potential of the technique in this area. The application areas outlined include polymer and biological materials, minerals and glasses, single crystals, ionic melts and complex ions in solution, simple covalent inorganic compounds and organic chemistry.

The book is highly recommended as it is timely, pleasingly written and an excellent technical production.

D. Thorburn Burns (Loughborough)

Treatise on Analytical Chemistry, édité par I. M. Kolthoff et P. J. Elving, Part I, Vol. 9, Wiley–Interscience, New York, 1972, xv + 552 pp., price £12.00.

Ce 9ème volume comprend deux parties: la section D-6 intitulée *Méthodes radioactives* est composée de 5 chapitres: Méthodes d'analyse radioactive et isotopique—Réactions nucléaires: identification et détection—Séparations radiochimiques—Technique des traces—Analyse par activation, et la section E: *Application à la mesure* dont les titres principaux sont: "Combinaisons" des propriétés chimiques et physiques pour l'identification et l'analyse—l'Analyse de traces: aspects essentiels—Détermination de la pureté.

Ce volume renferme une quantité considérable de chapitres dont l'un des plus originaux est celui qui met en rapport les propriétés physiques et le comportement chimique des systèmes simples et complexes, relation entre l'index de réfraction, la viscosité, la réfraction, la densité ou le point de fusion d'une part, et la composition chimique des mélanges d'autre part.

Puis les méthodes de séparations sont énumérées telles que: distillation, extraction, cristallisation, chromatographie liquide, diffusion thermique.

Un important chapitre donne les méthodes physiques d'analyse de substances à haut poids moléculaire.

Cette partie est bien traitée, c'est une synthèse de l'ensemble des méthodes nécessaires aux chimistes pour l'étude entre autres des produits naturels tels que les pétroles et les huiles.

Dans la 1ère partie, les méthodes radioactives sont bien développées. L'introduction est fort bien présentée et donne de façon claire les bases théoriques de la radioactivité et les propriétés des noyaux ainsi que la production des radionucléides. Peut-être les auteurs auraient-ils pu s'attarder un peu sur la partie chimique de l'analyse par activation. Ils ne donnent pas de références bibliographiques très récentes sur cette dernière méthode.

Comme pour les précédents, ce volume a été rédigé par 10 spécialistes parmi les plus distingués de l'Université et de la grande Industrie. C'est dire qu'on y trouve les méthodes et techniques les plus récentes. Cet ouvrage montre pour ceux qui en doutent encore l'importance que prend de nos jours cette discipline.

Denys Monnier (Genève)

PUBLICATIONS RECEIVED

R. Reuber, H. Wellens and K. Gruss, *Chemikon* (*Chemie in Übersichten*) (in German), Umschau Verlag, Frankfurt-am-Main, 1972.

Volumes I, II, V and VI of this series have now appeared. Volume I deals with the elements and the electronic shells of atoms; Volume II with radioactive elements, the development of knowledge about the atom, and chemical formulae; Volume V with the classification of organic compounds, nomenclature, and aromatic compounds; Volume VI with different types of organic syntheses. These small paperbacks should be very useful for revision work.

E. E. Aldridge, *Acoustical Holography*, Merrow Monographs, Practical Science Series, edited by J. G. Cook, Merrow Publishing Company, Watford, England, 1971, v+40 pp., price £1.25 ($4.00).

This small book is written at an elementary level, and contains chapters on the Theory of holograms, Acoustical holograms, Practical aspects, and Uses. An appendix contains information on synthetic aperture scans. The book is also available as a paperback.

M. A. Brown, *X-Ray Methods*, Merrow Monographs, Laboratory Methods Series, edited by D. F. G. Pusey and L. C. Roselaar, Merrow Publishing Company, Watford, England, 1971, iv+58 pp., price £1.25 ($4.00).

This text deals with the application of X-ray methods in quantitative and qualitative analysis, and in studies of particle size, degree of polymer crystallinity, preferred orientation, and low-angle scattering.

J. Manenc, *Thermodynamique Structurale des Alliages*. Collection SUP, edited by J. Benard (in French), Presses Universitaires de France, Paris, 1972, 195 pp.

This paperback deals, at a level suitable for undergraduate students, with the thermodynamics of alloys in equilibrium and non-equilibrium states.

Absorption Spectra in the Ultraviolet and Visible Region, Edited by L. Lang, Vol. XVI, Akademiai Kiado, Budapest, 1972, 400 pp. + indexes, price £7.00.

This volume contains spectra for a further 367 compounds.

J. D. Fast, *Interaction of Metals and Gases. Vol. 2. Kinetics and Mechanisms*, Philips Technical Library, Macmillan Press, Ltd., London, 1972, ix + 318 pp., price £10.00.

This book, written by the chief metallurgist of the Eindhoven Philips laboratories, deals almost entirely with the behaviour of gases in the interior of metals. Separate chapters cover solutions of gases in metals, diffusion in interstitial alloys, internal friction of metals, the Snoėk effect, and interaction of interstitials and other lattice imperfections. The text is intended for metallurgical students, industrial metallurgists and chemists.

R. M. Scott, *Thin-layer Chromatography Abstracts. 1968–1971*, Ann Arbor Science Publishers Inc., Ann Arbor, Mich., Distributed by J. Wiley and Sons, Inc., London–New York, 1972, 395 pp., price £6.20.

This book, produced lithographically to save time and cost, contains some 1200 abstracts of papers published during the period 1968 to the beginning of 1971. The abstracts are arranged under 23 headings, mainly covering different types of organic compounds, *e.g.* steroids, carbohydrates, alkaloids, alcohols, etc.

Proceedings of the Third Symposium on Coordination Chemistry, Edited by M. T. Beck, Akademiai Kiado, Budapest, 1971, Vol. 1, 525 pp., price £6.00; Vol. 2, 287 pp., price £2.75.

These volumes contain the proceedings of the symposium held at Debrecen, Hungary in April, 1970. The first volume contains the 48 papers which were presented, and the second contains the 5 plenary lectures and extensive discussions of the original papers.

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