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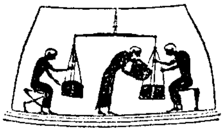

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is attached to work dealing with the principles of analytical chemistry in which experimental materi
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hitherto widely scattered material are considered for publication, but should be critical. Original pa
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which are critical commentaries on some aspect of analytical chemistry and deal with topics such as
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LOUIS GORDON MEMORIAL AWARD

THE Editorial Board and the Publisher of TALANTA have great pleasure in announcing that the Louis Gordon Memorial Award for 1970, for the best-written paper published that year in TALANTA, has been made to Mrs. Thelma Meites and Professor Louis Meites for their paper "Theory of Titration Curves—VII: The Properties of Derivative Titration Curves for Strong Acid–Strong Base and other Isovalent Ion-Combination Titrations," *Talanta*, 1970, **17**, 525.

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E. PUNGOR

and would like to record their sincere thanks for the help given by

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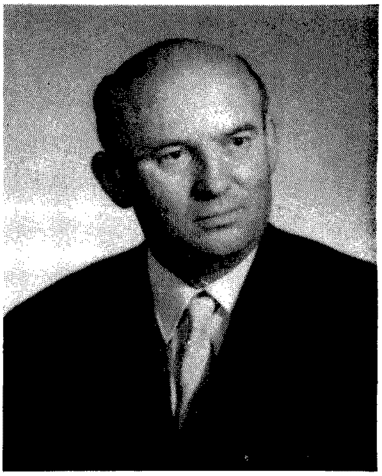
who retire from the Board.

Professor E. PUNGOR was born on 30 October 1923 in Vasszécsény, Hungary. He studied chemistry at the Pázmány Péter University in Budapest, where he got his diploma *summa cum laude* in 1948. A year later he took his doctor's degree, also *summa cum laude*. He became Candidate of Chemical Sciences in 1952 and Doctor of Chemical Sciences in 1956. In 1967 he was elected corresponding member of the Hungarian Academy of Sciences. After completing his university studies he worked with Professor Schulek in the Institute for Inorganic and Analytical Chemistry at the Eötvös University in Budapest, first as lecturer, later as senior lecturer and reader. He was appointed as professor in 1963 in the Department of Analytical Chemistry at the University of Veszprém. Since 1 August 1970 he has been head of the Institute for General and Analytical Chemistry of the Technical University in Budapest. He is a member of many scientific committees and editorial boards in Hungary and abroad (and chairman of some).



Professor PUNGOR's main scientific activities are in the field of instrumental analysis, first of all in electrochemistry and optical methods. Based upon his inventions, automatic titrimeters, oscillotitrators, etc., are produced in Hungary. He developed new theories concerning ion-selective membrane electrodes. His new types of electrode are commercially available and are successfully used world-wide. His books published in Hungarian and in English are *Oscillometry and Conductometry* (Akad. Kiadó, Budapest 1963, Pergamon Press, Oxford, 1965) and *Flame Photometry Theory* (Akad. Kiadó, Budapest 1962, Van Nostrand, London, 1967). His scientific publications number about 280 and cover almost every field of analytical chemistry (indicators, potentiometry, flame photometry, atomic absorption, high-frequency titrations, polarography, spectrophotometry etc.).

Professor PUNGOR is married and has three children, aged 19, 17 and 12. His only hobby is instrumentation.

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COULOMETRIC MICRODETERMINATION OF WATER

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(*Received* 3 *September* 1970, *Accepted* 9 *October* 1970)

Summary—An electroanalytical method for the determination of small amounts of water by controlled potential coulometry has been devised. Excess of iodine is produced coulometrically in a Karl Fischer reagent, the sample is added, and after complete reaction the remainder of the iodine is reduced. The number of coulombs consumed in the cell reaction is determined by integration of the current by means of an electronic integrator. Karl Fischer reagents of various compositions were checked to find the most satisfactory conditions and a special electrolysis cell for water determination was constructed entirely in glass and Teflon. Samples containing 0·1–2 mg of water were added and determined with an accuracy of ±0·15%. The analysis times were 3–12 min.

ACCURATE determination of small amounts of water (<1 mg) has caused considerable difficulties, which may easily be seen in the relevant literature.[1] A coulometric method using Karl Fischer (*KF*) reagent has been developed by Meyer and Boyd.[2] They generated iodine electrolytically in a depleted *KF* reagent by constant current until the water in the sample was consumed, and the end-point was determined by a "dead stop" technique. This method has since been modified and improved.[3,4]

Rechnitz and Srinivasan[5] pre-electrolysed a *KF* reagent at controlled potential until most of the iodide in the solution became oxidized. The sample containing water was added and the iodide produced in the reaction was also oxidized at the same potential. The electrolysis current was integrated by a slope intercept method. The time required for a complete determination of 1–2 mg of water was about 50 min and the accuracy was rather low.

A coulometric method at controlled potential has also been proposed by Lindbeck and Freund.[6] By producing a known excess of iodine coulometrically in a spent *KF* reagent containing the sample, followed by reduction of the iodine and integration of the electrolysis current, the water content in the sample was determined; 0·1-ml samples containing 10–82 μg of water were analysed.

In this paper the determination of water by coulometry at controlled potential has been investigated further. A specially adapted *KF* reagent and a new electrolysis cell have been developed. Principally our method is as follows: all iodine in a *KF* reagent is reduced to iodide in an electrolysis cell with a rotating platinum cathode. After that, the current direction is changed and a known amount of iodine is generated at the rotating platinum electrode which now is the anode. The amount of electritcity is measured by an electronic integrator. The sample is then added and consumes most of the iodine. The current direction is changed again, the excess of iodine is reduced and the amount of electricity required is subtracted from that used to generate the iodine.

EXPERIMENTAL

Electrolysis cell

Several electrolysis cells have been constructed and tested and the most efficient cell is shown in Fig. 1. The working compartment consists of a B45 ground joint and a Teflon plug, which gives

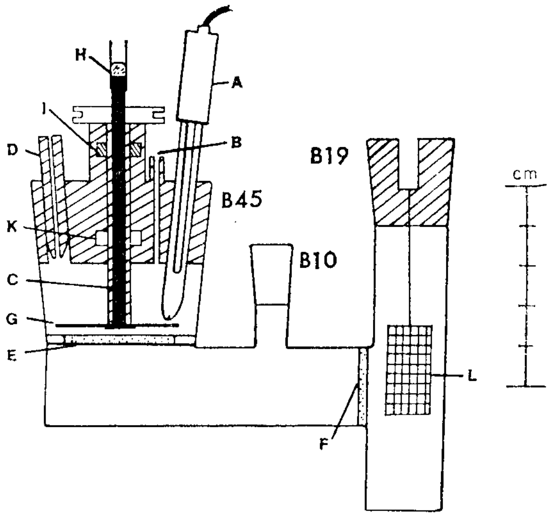

Fig. 1.—Electrolysis cell.
A—Reference electrode. *B*—Nitrogen inlet. *C*—Electrode axis. *D*—Nitrogen outlet and sample addition. *E*, *F*—Glass frits (G4). *G*—Working electrode. *H*—Mercury pool. *I*—Stainless-steel ball-bearing. *K*—Nylon packing. *L*—Counter electrode.

a gas-tight fit in the joint. The Teflon plug has four holes intended for reference electrode (*A*), nitrogen inlet (*B*), axis for the working electrode (*C*) and Teflon stopper (*D*). The last is provided with a hole for nitrogen outlet and sample addition and is removed for refilling the compartment. The liquid volume in the compartment is about 10 ml. The bridge compartment, bounded by two porosity 4 glass frits (*E*, *F*) is filled with 1*M* sodium perchlorate in absolute methanol and a small excess of *KF* reagent to prevent moisture from entering the working compartment. Refilling of electrolyte is done through the B10 socket. The counter-electrode compartment consists of a B19 socket fitted with a Teflon plug and electrode holder. The electrolyte in this compartment consists of equal volumes of *KF* reagent and 1*M* sodium perchlorate in absolute methanol.

Electrodes

The working electrode (*G*) is a 36-mesh round platinum gauze, 35 mm in diameter, which is rivetted on a 15 mm long platinum rod (4 mm diameter). The platinum rod is soldered to a stainless-steel rod fitted with a mercury contact (*H*) at the top. The whole shaft of the electrode is Teflon-covered to protect the steel from the solution. A stainless-steel ball-bearing (*I*) and a nylon packing (*K*) serve to give the shaft good packing and free the rotation from vibration. The rotational speed of the shaft can be varied stepwise between 200 and 1500 rpm by a transmission system and a stirring motor (Radiometer Type M 22).

The reference electrode is a calomel electrode (Radiometer K 901) filled with a saturated lithium chloride solution in methanol. The counter-electrode (*L*) consists of a 36-mesh platinum gauze with an area of $1{\cdot}2 \times 10^3$ mm^2.

Apparatus

The controlled-potential electrolysis system used is illustrated in Fig. 2 and is based on principles devised by Kelley *et al.*[7] and by Booman,[8] and modified by Johansson.[9]

The potentiostat for controlling the voltage difference is constructed round an operational amplifier (Nexus SL 26) and an ammeter with logarithmic scale is used in order to cover the whole operating range without changing scale. The number of coulombs consumed in the cell reactions is determined by integration of the current, by means of a chopper-stabilized operational amplifier (G. A. Philbrick S.P. 656) with 10-μF feedback capacitor. The read-out device is a compensation bridge, and the analysis time is measured with an electric timer. Calibration of the integrator by means of time and voltage gave an error of less than 0·05% over the whole range.

Chemicals

Lithium chloride dried in a tube-oven at 275° for 24 hr. Sodium perchlorate dried at 175° for 24 hr. Methanol ($<0{\cdot}03\%$ H_2O). Pyridine ($<0{\cdot}02\%$ H_2O). Sulphur dioxide ($>99{\cdot}9\%$ pure).

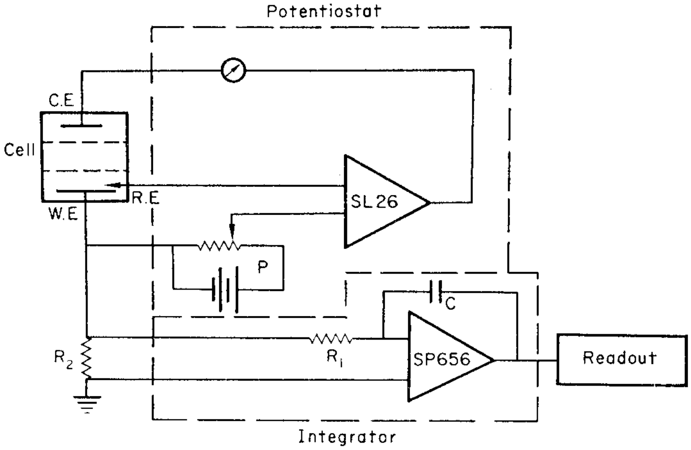

FIG. 2.—Electronic circuitry.
W.E. (working electrode), R.E. (reference electrode), C.E. (counter electrode), P (potentiometer), C (capacitor, 10 μF), R_1 (resistor, 1 MΩ), R_2 (resistor, 10 Ω).

Nitrogen (purity >99·9%) passed over copper at 500° and then through Ascarite, Dehydrite and phosphorus pentoxide before entering the cell.

Methanol-water solutions

Methanol containing <0·03% water was dried over molecular sieves (0·3 nm) and the water content after drying was found to be 0·0075%. Between 100 and 1000 mg of water were then added by syringe microburette to the methanol in 10-ml volumetric flasks, which were then placed in desiccators containing phosphorus pentoxide.

Procedure

Every trace of moisture was first removed from the working compartment by generating iodine coulometrically and rotating the electrode at such a speed that the whole compartment was totally washed with the reagent. If the cell had not been used for some time the removal of the water would take about half an hour, but when it was used daily a few minutes was enough, provided the cell had been stored filled with *KF* reagent. The speed was then decreased to 500 rpm and the excess of iodine was reduced until the current reached a stable residual value (5–10 μA). After this start-up the following sequence of operations was used for each sample:

1. Reset the integrator and timer.
2. Produce an excess (15–25%) of iodine by electrolytic oxidation.
3. Add the sample and allow 10–30 sec for complete reaction.
4. Reduce the excess of iodine.
5. Read the integrator and timer.
6. Repeat steps 1–5 without sample addition (blank test).

The actual loss of iodine per minute from the *KF* reagent is calculated from the blank. (If the excess of iodine in step 2 is too low the next blank tends to be somewhat too high, on account of incomplete reaction between water and iodine.) A correction is calculated from the blank test and subtracted from the reading (see 5 above) and the result obtained is converted into μg of water as follows:

$$9{\cdot}008 \times \frac{10^3 A \,.\, U_c}{F} = \mu\text{g H}_2\text{O}$$

where 9·008 = equivalent weight of water, A = factor for integrator components (0·9948 sec/ohm), F = Faraday constant (96487 C/mole), U_c = integrator read-out, corrected (mV).

Samples ranging from 10 to 200 μl were added by syringe microburette with a Mauser micrometer (2278 NH Mauser-Messzeug G.m.b.H.) fixed on a rigid steel stand. Sample volumes were accurate to $\pm 5 \times 10^{-6}$ ml.

RESULTS

KF reagents with compositions ranging from 0·05 to 1*M* in iodine, 0·1 to 5*M* in pyridine and 0·05 to 1·5*M* in sulphur dioxide, as solutions in methanol, were checked to get the most satisfactory conditions. High concentrations of pyridine prolonged the analysis time and the stability of the reagent decreased with increasing concentrations of sulphur dioxide. We found that a reagent with the following composition gives the best result: 0·1*M* iodine, 0·1*M* sulphur dioxide and 0·5*M* pyridine in methanol. These concentrations are not very critical and small deviations do not matter. Contrary to Lindbeck and Freund, we used iodine instead of sodium iodide when preparing our reagent as we observed that the use of sodium iodide caused precipitation which to some extent increased the analysis time.

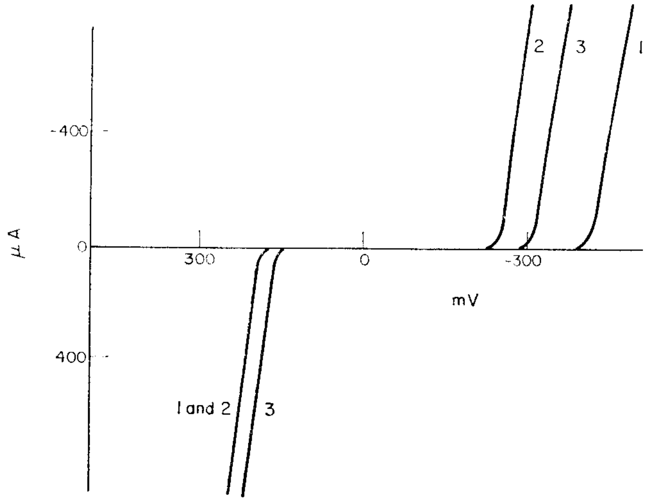

FIG. 3.—Current-voltage curves.
1—0·1*M* I_2 solution in methanol.
2—0·1*M* I_2 + 0·1*M* SO_2 solution in methanol.
3—0·1*M* I_2 + 0·1*M* SO_2 + 0·5*M* pyridine solution in methanol.

We built up our reagent stepwise and studied each step by means of current–voltage measurements *vs.* a calomel electrode filled with saturated methanolic lithium chloride solution. Figure 3 shows the curves for oxidation of iodide to iodine at positive potentials and the reduction of pyridinium ion and solvent at negative potentials. From these curves the working potentials for the oxidation and reduction steps were determined to be +350 mV and 0 mV, respectively.

Oxidation and reduction of the iodine–iodide couple in a solution of methanol and pyridine resulted in correct values but for corresponding measurements in a *KF* reagent the number of coulombs for the reduction step was somewhat lower than for the oxidation step. The reason for this loss of iodine from the reagent is probably uncontrollable side-reactions involving reduction of iodine[10] and possibly also minute quantities of moisture entering the cell. This loss of iodine is, however, small and reproducible for our reagent and as the apparatus works at relatively high currents which permit short analysis times to be used, we have this loss under complete control, as can be seen from the following example: when 25·00 μmole of iodine were produced by oxidation the reduction gave 24·80 ± 0·01 μmole. The oxidation time was 140 sec and the reduction time 250 sec. The nitrogen flow through the cell was 10 ml/min.

For an electrode reaction which is carried out at a potential at which the reaction rate is limited by the rate of mass transfer of the electroactive species, in this case iodine, to the electrode, the electrolysis current decays (according to Lingane[11]) as follows:

$$i_t = i_0 \cdot e^{-pt}$$

where i_0 = initial current, i_t = the current at time t, $p = f$ (electrode dimensions, solution volume, cell-geometry and mass transfer).

The electrolysis time decreases with increasing value of p. By plotting log i *vs.* time a straight line is obtained from which p can be determined. The cell used gave a p-value of 2·5 min^{-1} with newly prepared solutions, cleaned filters and electrodes. The solution volume in the cell was about 10 ml and the speed of the electrode 500 rpm. Increase of the speed had no effect on the p-value.

After some weeks of use of the electrode the p-value had decreased somewhat, depending on salt precipitates in the filters and the formation of organic polymerization products on the platinum gauzes, which decreased the rate of transfer. When the p-value was below 2·0 min^{-1} the cell was cleaned.

From Tables I and II the effect of the analysis time on the results is apparent. A determination of 100 μg of water takes about 3 min and a determination of 2000 μg about 12 min. The loss of iodine from the reagent is about 0·5 μg/min, calculated as water, so it is necessary to keep the analysis times under control so that the blank adjustment will be as correct as possible.

TABLE I.—COULOMETRIC DETERMINATION OF WATER IN SOME ORGANIC SOLVENTS

Solvent	Solvent added, μl	H_2O found, μg	Number of determinations	Standard deviation, μg
Methanol	10	99·9	6	$0{\cdot}1_8$
	20	199·6	5	$0{\cdot}3_0$
	40	399·3	5	$0{\cdot}3_4$
Cellosolve	10	103·7	6	$0{\cdot}2_5$
	20	207·1	6	$0{\cdot}3_5$
	40	414·1	6	$0{\cdot}5_0$
Acetonitrile	10	155·9	4	$0{\cdot}2_5$
	20	311·7	5	$0{\cdot}4_0$
	40	623·1	5	$0{\cdot}5_2$
Dimethylsulphoxide	10	196·5	6	$0{\cdot}3_0$
	20	393·4	7	$0{\cdot}3_5$
	40	786·8	7	$0{\cdot}5_0$

DISCUSSION

Lindbeck and Freund[6] stated that they could not use higher currents than 10 mA in the reduction of iodine or the results would be high. They also indicated that if the reduction current was kept below 10 mA correct values were obtained even if the cathode potential was varied by as much as 300 mV.

TABLE II.—COULOMETRIC DETERMINATION OF WATER IN METHANOL

H_2O calculated, μg	H_2O found,* μg	Difference	
		μg	%
100·30	100·07	−0·23	−0·23
116·82	116·93	+0·11	+0·09
144·32	143·99	−0·33	−0·22
199·79	199·48	−0·31	−0·16
395·02	394·77	−0·25	−0·06
592·53	592·24	−0·29	−0·05
799·16	800·03	+0·87	+0·11
843·95	844·86	+0·91	+0·11
1044·5	1042·9	−1·6	−0·15
1688·0	1685·1	−2·9	−0·17
1912·4	1910·2	−2·2	−0·12

* Mean value of 3 determinations.

We have often reduced iodine with initial currents of more than 50 mA and still obtained correct values. The cell used by Lindbeck and Freund had probably a much lower rate of mass transfer, as the stirring was produced by nitrogen bubbling at the working electrode. This leads to the important disadvantage that they could determine only very small amounts of water within reasonable times. Further, the accuracy depends on the rate of electrolysis, as the influence of side-reactions and the loss of iodine through evaporation are proportional to time.

Better electronic circuitry and a more efficient electrolysis cell are under construction to permit shorter analysis times and consequently lower loss of iodine, which will lead to higher accuracy and the possibility of determining much smaller amounts of water (smaller by 1 or 2 orders of magnitude) with the same accuracy.

Acknowledgement—The authors thank Professor Gillis Johansson for valuable help and discussions and Dr. Peter Sellers for correcting the English. The authors are also very much indebted to the Swedish Board for Technical Development for financial support.

Zusammenfassung—Ein elektroanalytisches Verfahren zur Bestimmung kleiner Wassermengen durch Coulometrie bei geregeltem Potential wurde ausgearbeitet. Ein Jodüberschuß wird in Karl-Fischer-Reagens coulometrisch erzeugt, die Probe zugegeben und nach Beendigung der Reaktion das restliche Jod reduziert. Die Anzahl der bei der Reaktion in der Zelle verbrauchten Coulomb wird durch Integration des Stroms mit Hilfe eines elektronischen Integrators ermittelt. Es wurden Karl-Fischer-Reagenslösungen verschiedener Zusammensetzungen untersucht, um die optimalen Bedingungen zu finden, und es wurde eine besondere Elektrolysezelle für die Wasserbestimmung ganz aus Glas und Teflon konstruiert. Proben mit 0,1–2 mg Wasser wurden zugegeben und mit einer Genauigkeit von ±0,15% bestimmt. Die Analysenzeiten betrugen 3–12 min.

Résumé—On a élaboré une méthode électroanalytique pour la détermination de petites quantités d'eau par coulométrie à potentiel contrôlé. Un excès d'iode est produit coulométriquement dans un réactif de Karl Fischer, on ajoute l'échantillon, et après réaction complète, on réduit le restant de l'iode. Le nombre de coulombs consommés dans la réaction en cellule est déterminé par intégration du courant au moyen d'un intégrateur électronique. On a contrôlé des réactifs de Karl Fischer de compositions variables pour trouver les

conditions les plus satisfaisantes et l'on a construit une cellule d'électrolyse spéciale pour la détermination de l'eau, entièrement en verre et Teflon. On a ajouté et déterminé avec une précision de ±0,15% des échantillons contenant 0,1–2 mg d'eau. Les temps d'analyse sont de 3–12 mn.

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THE ERROR IN ABSORPTION MEASUREMENTS, CAUSED BY THE USE OF NON-MONOCHROMATIC LIGHT—I

PARABOLIC FUNCTIONS

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Summary—The errors in absorption measurements in spectrophotometry, caused by the use of non-chromatic light, have been calculated. Parabolic functions have been assumed for the wavelength-dependence of the intensity of the incident light falling on the cell and of the absorbance of the compound measured. Results of the calculations may be used to predict non-linearity of absorbance-concentration curves or photometric titration curves.

SPECTROPHOTOMETRIC errors may arise because of the use of non-monochromatic light. Kortüm[1] has discussed the consequences in the simple case that the incident light consists of only two components. Goldring *et al.*[2] give some approximate calculations of the error for some cases when the intensity of the incident light is a triangular function of wavelength. Asmus[3] gives a procedure which introduces less approximations than the one given below, but for each problem a special calculation must be made and general conclusions cannot be drawn.

In the present paper formulae are derived which may have a more general applicability. Results of the calculations made are given for the error in the absorption measurements in a number of cases that may be met in practice.

DERIVATION OF EQUATIONS

Assumptions

For convenience the wavelength λ at the maximum (or minimum) absorption of the component measured (Fig. 1) is taken as reference and assigned the value zero. The absorbance at this value $\lambda = 0$ is E_0; at other wavelengths E_λ is often given in fair approximation by

$$E_\lambda = E_0(1 - \beta\lambda^2) \tag{1}$$

In this function, β (positive for a maximum; negative for a minimum) is a measure of the sharpness of the absorption-curve. For $\beta > 0$ the half-bandwidth is defined in the usual way as the wavelength region where E_λ varies between $\frac{1}{2}E_0$ and E_0. The value of the half-bandwidth is $\sqrt{2/\beta}$. For negative β-values a half-bandwidth with physical significance cannot be defined in the usual way. Therefore, for the purpose of this paper it is arbitrarily defined as the wavelength region where E_λ varies between E_0 and $1\frac{1}{2}\, E_0$, because with this definition it has the same value $\sqrt{2/\beta}$ as in the case for $\beta > 0$. Of course E_λ cannot be negative and therefore zero-value is assigned to E_λ for values of β and λ where equation (1) would suggest negative values for E_λ (see Fig. 1).

For the intensity of the light falling on the cell, $I_\lambda{}^0$ (Fig. 2), the function

$$I_\lambda{}^0 = I^0\{1 - \alpha(\lambda - z)^2\} \tag{2}$$

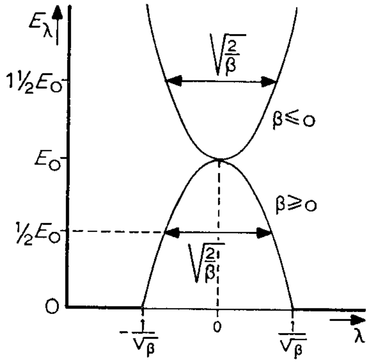

FIG. 1.—Absorbance E_λ as a function of wavelength λ.

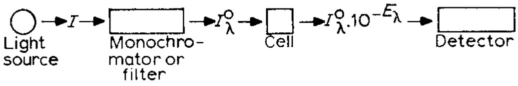

FIG. 2.—Light intensity at successive places in the spectrophotometer.

was assumed, where I^0 is the maximum light-intensity falling on the cell; z is the difference in wavelength units between the maximum of the light-intensity curve (Fig. 3) and the maximum or minimum of the absorption-curve (Fig. 1). Here α is positive only, the half-bandwidth is $\sqrt{2/\alpha}$ and $I_\lambda{}^0 = 0$ at $\lambda = z \pm 1/\sqrt{\alpha}$ (Fig. 3). Strictly speaking, the wavelength dependence of the light source intensity I and of the detector sensitivity should also be considered. In many cases, especially if the wavelength range used is not too large, the combined influence of both factors may be neglected, and function (2) applies to the filter or monochromator only.

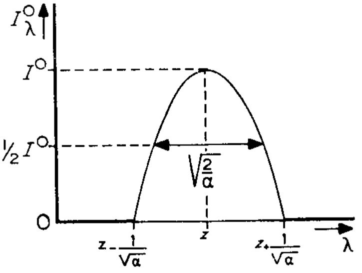

FIG. 3.—Intensity of incident light $I_\lambda{}^0$ as a function of wavelength.

Function (2) is in good agreement with the absorption curve of many filters, and does not give much deviation from the (roughly triangular) function for a prism or grating monochromator.

Losses of light intensity independent of the wavelength, λ, are not important; the presence of stray light has been neglected.

Calculations

For the calculations and the interpretation, introduction of the quantities b, k, A and B is useful:

$$b = z\sqrt{\alpha} \tag{3}$$

$$k = \sqrt{\frac{\alpha}{|\beta|}} \tag{4}$$

$$A = 1 - \alpha\left(\lambda - \frac{b}{\sqrt{\alpha}}\right)^2 \tag{5}$$

$$B = 10^{-E_0(1-\beta\lambda^2)} \tag{6}$$

The physical meaning of b is:

$$b = \frac{I^0 - \lambda_{E^0}}{\text{half-bandwidth of } I_\lambda{}^0 \text{ curve}} \cdot \sqrt{2} \tag{7}$$

Calculations were made only for $b \geqslant 0$. From considerations of symmetry it is clear that the same results are found for negative values of b.

The physical meaning of k is:

$$k = \frac{\text{half-bandwidth of } E_\lambda \text{ curve}}{\text{half-bandwidth of } I_\lambda{}^0 \text{ curve}} \tag{8}$$

(when using this formula, take heed of the definition of the half-bandwidth when $\beta < 0$).

The measured absorbance E_m, is a mean value over the wavelength region considered, and may be given by the general formula:

$$E_\text{m} = \log \frac{\int I_\lambda{}^0 \,\mathrm{d}\lambda}{\int I_\lambda{}^0 \,.\, 10^{-E_\lambda} \,\mathrm{d}\lambda} \,. \tag{9}$$

The relative error is:

$$\frac{\Delta E}{E_0} = \frac{E_\text{m} - E_0}{E_0} \,. \tag{10}$$

Several cases should be distinguished, each giving different limits of integration in equation (9).

I. Case I, shown in Fig. 4, shows the situation with $\beta \leqslant 0$. This is the not very common case, where a minimum of the absorption curve is used. For each value of $I_\lambda{}^0$, a positive value of E_λ does exist and

$$E_\text{m} = \log \frac{\int_{(b-1/\sqrt{\alpha})}^{(b+1/\sqrt{\alpha})} A \,\mathrm{d}\lambda}{\int_{(b-1/\sqrt{\alpha})}^{(b+1/\sqrt{\alpha})} AB \,\mathrm{d}\lambda} \,. \tag{11}$$

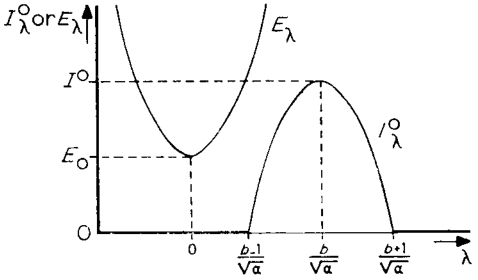

FIG. 4.—Case I, $\beta \leqslant 0$.

II. In the more common case that $\beta \geqslant 0$, several subcases must be distinguished.

II.1. See Fig. 5. In this case formula (11) is also applied.

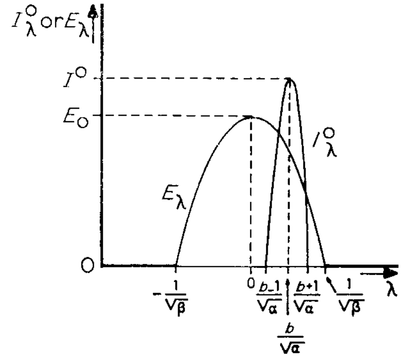

FIG. 5.—Case II. 1.

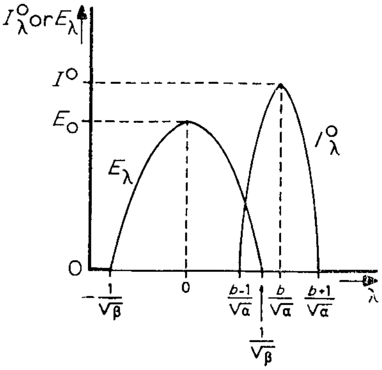

FIG. 6.—Case II. 2.

II.2. See Fig. 6. In this case no light is absorbed over the wavelength region from $1/\sqrt{\beta}$ to $(b+1)/\sqrt{\alpha}$ and

$$E_m = \log \frac{\int_{(b-1/\sqrt{\alpha})}^{(b+1/\sqrt{\alpha})} A\,\mathrm{d}\lambda}{\int_{(b-1/\sqrt{\alpha})}^{(1/\sqrt{\beta})} AB\,\mathrm{d}\lambda + \int_{(1/\sqrt{\beta})}^{(b+1/\sqrt{\alpha})} A\,\mathrm{d}\lambda} \cdot \qquad (12)$$

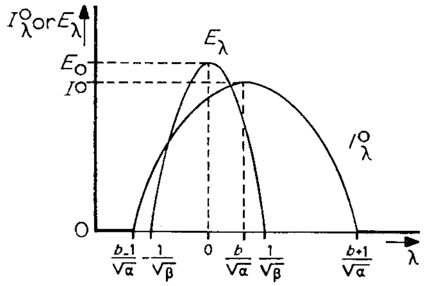

FIG. 7.—Case II. 3.

II.3. See Fig. 7. In this case no light is absorbed at either end of the intensity spectrum and

$$E_m = \log \frac{\int_{(b-1/\sqrt{\alpha})}^{(b+1/\sqrt{\alpha})} A \, d\lambda}{\int_{(b-1/\sqrt{\alpha}}^{(-1/\sqrt{\beta})} A \, d\lambda + \int_{(-1/\sqrt{\beta})}^{(1/\sqrt{\beta})} AB \, d\lambda + \int_{(1/\sqrt{\beta})}^{(b+1/\sqrt{\alpha})} A \, d\lambda} . \tag{13}$$

II.4. See Fig. 8. In this case no light is absorbed at any wavelength, E_m is always zero and the error is always 100%.

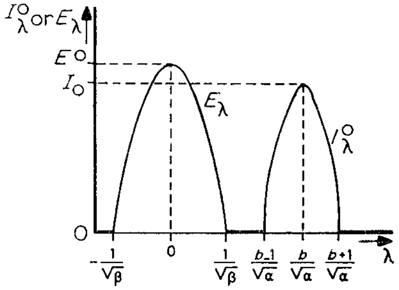

FIG. 8.—Case II. 4.

RESULTS

To each of a number of combinations of α, β and b, one of the formulae (11), (12) or (13) was applied, and $\Delta E/E_0$ was calculated for $E_0 = 0{\cdot}05$; $0{\cdot}1$; $0{\cdot}5$; 1; 2. Calculations were made by an EL X 8 computer. Results have been summarized in Tables I–III.

Not unexpectedly it was found that it is not the individual values of α and β that are important for the results, but the quotient $\alpha / |\beta| = k^2$.

The values chosen for k and b were adapted as far as possible to cases that may be met in practical measurements.

The tables show that in many cases the relative error is practically independent of the absorbance, a very favourable situation for calibration curves, and photometric titration curves. In many other cases the relative error is practically a linear function of absorbance. In relatively few cases is the relation between the relative error and the

TABLE I.—ERRORS IN THE ABSORPTION MEASUREMENT, FOR POSITIVE β-VALUES

b	$k = \sqrt{\frac{\alpha}{\|\beta\|}}$					
	10^2	$10^{1\cdot5}$	10^1	$10^{0\cdot5}$	1	$10^{-0\cdot5}$
100	>90	>90	>90	>90	>90	>90
50	25·0	>90	>90	>90	>90	>90
20	4·00	40·1	>90	>90	>90	>90
10	1·00	10·0	>90	>90	>90	>90
5	0·25	2·52	25·2 25·7	>90	>90	>90
2	0·04	0·42	4·20 4·28	42·2 49·9	>90	>90
1	0·01	0·12	1·20 1·22	12·05 14·13	*	>90
0·5	0·00	0·05	0·45 0·46	4·51 5·12	*	77·7 92·3
0·2	0·00	0·02	0·24	2·40 2·59	*	*
0	0·00	0·02	0·20	2·00 2·11	20·3 34·6	*

The values are given in per cent ($-100\ \Delta E/E_0$).

If two values are given, the first value gives the error at $E_0 = 0{\cdot}05$, the second at $E_0 = 2{\cdot}0$. In all these cases the error depends practically linearly on the absorbance (deviation from linearity <1% absolute).

* See Table III.

TABLE II.—ERRORS IN THE ABSORBANCE MEASURED, FOR NEGATIVE β-VALUES

b	$k = \sqrt{\frac{\alpha}{\|\beta\|}}$					
	10^2	$10^{1\cdot5}$	10^1	$10^{0\cdot5}$	1	$10^{-0\cdot5}$
100	>90	—	—	—	—	—
50	25·0	—	—	—	—	—
20	4·00	—	—	—	—	—
10	1·00	10·0	100·1 98·4	>90	>90	>90
5	0·25	2·52	25·2 24·7	>90	>90	>90
2	0·04	0·42	4·20 4·13	4·18 35·5	>90	>90
1	0·01	0·12	1·20 1·18	11·9 10·2	*	>90
0·5	0·00	0·04	0·45 0·44	4·49 3·99	*	>90
0·2	0·00	0·02	0·24	2·40 2·23	*	*
0	0·00	0·02	0·20	2·00 1·90	*	*

Units and symbols as in Table I. The values are given in per cent ($+100\ \Delta E/E_0$).

TABLE III.—ERRORS IN THE ABSORBANCE MEASURED, FOR CASES MARKED WITH AN ASTERISK IN TABLES I AND II

E	β negative $k = \sqrt{\frac{\alpha}{\|\beta\|}}$						β positive $k = \sqrt{\frac{\alpha}{\beta}}$				
	$k = 1$				$k = 10^{-0.5}$		$k = 1$			$k = 10^{-0.5}$	
	$b = 1$	0·5	0·2	0	0·2	0	1	0·5	0·2	0·2	0
0·05	115	43·6	23·6	19·7	202	176	73·2	39·6	24·0	71·1	69·9
0·1	111	42·3	23·1	19·5	174	157	73·8	40·4	24·4	72·0	70·7
0·2	103	39·8	22·3	19·0	138	129	75·1	42·1	25·3	73·6	72·4
0·5	83·4	33·8	20·2	17·6	89·0	85	78·5	47·2	28·3	77·9	76·8
1·0	63·7	26·9	17·5	15·7	58·5	56·7	83·0	55·6	34·1	83·3	82·4
2·0	44·4	19·3	13·8	12·8	36·5	35·6	88·5	69·0	47·4	89·4	88·8

The values are given as per cent: $-100\ \Delta E/E_0$ for positive β values, $+100\ \Delta E/E_0$ for negative β values.

absorbance of a more complicated nature. In analytical practice the tables may often be used to predict roughly the deviation from linearity of absorbance–concentration curves if the wavelength-dependence of the intensity of the light falling on the cell and of the light absorption of the compound measured are known. It seems reasonable to assume that the deviation from linearity is not sufficient to invalidate assumptions made in the calculations.

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Zusammenfassung—Die Fehler in der Extinktionsmessung in der Spektrophotometrie, verursacht durch Gebrauch von nicht-monochromatischem Lichte, wurden berechnet. Parabolfunktionen wurden angenommen für die Wellenlange-Abhängigkeit der Intensität des Auffallenden Lichtes, und für die Absorptionskurve der gemessenen Substanz. Aus den Resultaten der Berechnungen kann man die nichtlinearität von Extinktion-Konzentration Kurven oder photometrischen Titrationskurven vorhersagen.

Résumé—On a calculé les erreurs, causées par l'usage de lumière nonmonochromatique dans la mesure de l'extinction spectrophotométrique. On a supposé des courbes paraboliques pour l'intensité de la lumière incidente, et pour la courbe d'absorption du composé mésuré. Les résultats des calculs donnent la possibilité de prévoir une non-linearité des courbes extinction-concentrations, ou des courbes de titrages photométriques.

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DETERMINATION OF SILVER IN ORES AND METALLURGICAL CONCENTRATES BY A COMBINATION OF FIRE-ASSAY PRECONCENTRATION (USING TIN AS COLLECTOR) AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY*

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Summary—A new method is described for the determination of silver in ores and metallurgical concentrates. The procedure is based on collection of silver in a tin button during a fire assay fusion, and the subsequent determination by atomic-absorption spectrophotometry. The proposed method is rapid and free from inter-element interferences, and results obtained agree favourably with those obtained by alternative methods.

AN ANALYTICAL SCHEME for the determination of gold and the platinum-group metals in ores and metallurgical products was developed in the Mines Branch Laboratories.[1] This method, based on the collection of the precious metals with tin during the crucible fusion process of fire assaying, has been used for a number of years at the Mines Branch for the analysis of a wide variety of materials.

Because silver, in part, forms a soluble species (as do iridium and ruthenium[2,3]) when the tin assay button is treated with hydrochloric acid, the analytical scheme did not incorporate the means for determining this metal. However, because silver is the most common precious metal, it was clearly desirable to extend the tin-collection scheme to include silver.

This note describes a simple method for recovering silver from tin assay buttons, and subsequently determining this metal in a dilute hydrochloric acid solution by atomic-absorption spectrophotometry (AAS). Separation of silver from other precious metals is not required. The new method is considered to be simple, rapid, and more widely applicable than other methods for determining silver in complex ores and concentrates.

EXPERIMENTAL

Apparatus

Assay furnace, 15-kW *Globar type.*

Jelrus Handy-Melt electric furnace.

Techtron Atomic Absorption Spectrophotometer, Model AA-5. Operating parameters were as follows: hollow-cathode lamp current 3 mA; wavelength 328·1 nm; slit-width 100 μm; a 100-mm narrow-slit burner; air 166 kN/m^2 (24 psig); acetylene 69 kN/m^2 (10 psig). While aspirating distilled water, adjust the flow-meters to approximately 1·8 units for acetylene, and 7·0 units for air.

Reagents

Standard silver solution. Prepared by dissolving pure silver foil in dilute nitric acid (1 + 3), followed by dilution to 1 litre with approximately 10% v/v nitric acid.

Tin(IV) oxide. For all assay fusions, tin(IV) oxide obtained from British Drug Houses Ltd., was used, because this material consistently gave silver blank values of 0–30 μg/40 g of SnO_2.

Standard assay flux

Tin(IV) oxide	40 g
Sodium carbonate	50 g
Silica	17 g
Borax	10 g
Assay crucibles (A. P. Green)	40 g
Coke	6 g

Procedure

Preparation of tin assay buttons. The assay flux was used in the preparation of all tin assay buttons, and the fusions (for both synthetic and natural samples) were conducted at 1250° for 1·5 hr. All synthetic samples were prepared by salting the flux with 0·5 g each of Cu, Ni and Fe (as oxides) and with various aliquots of the standard silver solution in the manner described previously.[4] For the fusion of samples of certain metallurgical concentrates, containing more than 3 g of combined copper and nickel, 15–25 g of stick tin were added to the charge to lower the melting point of the resultant alloy.

Analysis of tin assay buttons. Each tin assay button, weighing approximately 25 g, was cleared of adhering slag, then placed in the Jelrus Handy-Melt furnace, from which air was purged by nitrogen delivered through a small Vycor tube placed directly over the button. The temperature was increased until the button became molten, (700°–1000°); the melt was then poured into water to granulate the alloy. Any large lumps of the alloy were easily reduced in size with snips.

After dissolution of the tin alloy in 150 ml of concentrated hydrochloric acid, the contents of the beaker were diluted with an equal volume of water. To precipitate silver from the hydrochloric acid solution, 0·5 g of tin powder was added while the solution was stirred with a polyethylene-coated electric stirrer. (Note—nickel and copper present in the tin button dissolve during acid treatment of the alloy, but only the copper and precious metals are reduced by the tin powder treatment. Iron, if present in the sample, is extracted into the assay slag during fusion.) After the mixture had been stirred for approximately 15 min, the solution was filtered by decantation through a pad of paper pulp prepared from Whatman No. 31 paper. The solids left in the beaker were dissolved in 25 ml of concentrated hydrochloric acid and 10 ml of 30% hydrogen peroxide. The beaker was then covered with a watch-glass, and the solution brought to the boil to ensure that all silver was in a soluble form. Any silver retained on the filter pad was dissolved by treatment with a solution of 10 ml of hydrochloric acid and 2 ml of hydrogen peroxide, and the solution was collected in the original sample beaker. To prevent possible blockage of the atomizer by particulate matter, the combined solution was filtered through a fast filter paper (No. 31) into a 200-ml volumetric flask. The filter paper was washed several times with water, and the combined filtrate and washings were made up to volume. The resultant solution for atomization is approximately $2M$ in hydrochloric acid.

For milligram quantities of silver, the solution obtained by dissolving the final residue was filtered into a 500-ml flask, and kept at approximately $3M$ hydrochloric acid concentration to prevent precipitation of silver as the chloride. An appropriate aliquot was taken, and adjusted to $2M$ in hydrochloric acid for atomization.

The calibration curves, based on various portions of standard silver solution, were linear from 0·1 to 4 ppm of silver, the range used.

Correction for silver in tin(IV) oxide. Because all batches of tin(IV) oxide tested in this laboratory were found to contain a significant concentration of silver, it is necessary to carry a "blank" (in duplicate) through the analytical scheme. The "blank" value is deducted subsequently from the silver values.

RESULTS

Recovery of silver from synthetic samples

To establish the efficiency of tin as a collector for silver during the crucible fusion, a number of flux charges were salted with known quantities of silver and base metal oxides, to simulate an ore sample, and then the charges were fused to produce buttons weighing approximately 25 g. The buttons were analysed for silver by the procedure given above. The results are given in Table I.

Results in Table I show that tin is an efficient collector for microgram and milligram quantities of silver during the crucible fusion. The result of test 3, in which the reduction step with tin powder was omitted, indicates that approximately 75% of the silver dissolves (probably as $AgCl_2^-$) during the treatment of the granulated button with hydrochloric acid.

TABLE I.—DETERMINATION OF SILVER IN SYNTHETIC SAMPLES

Test no.	Silver	
	Taken	Found
1	127 μg	130 μg
2	381 μg	390 μg
3	508 μg	130 μg*
4	635 μg	640 μg
5	5·08 mg†	5·1$_4$ mg
6	10·16 mg†	10·1$_6$ mg
7	15·24 mg†	15·3$_0$ mg

* Tin powder reduction step omitted.

† Aliquots of sample solution taken for atomization.

Because gold, platinum, palladium and rhodium are encountered most frequently in ores and concentrates containing (copper, nickel, iron) sulphides, it was necessary to determine the effect of these precious metals on the determination of silver. Accordingly, a number of synthetic samples were prepared by salting the flux with both the silver standard and various amounts of other precious metals. Tin buttons obtained were analysed for silver according to the procedure given above; the results are given in Table II.

TABLE II.—DETERMINATION OF SILVER IN SYNTHETIC SAMPLES CONTAINING OTHER PRECIOUS METALS

Test no.	Silver taken, μg	Precious metals taken, μg				Silver found, μg
		Pt	Pd	Rh	Au	
8	254	—	—	—	1260	260
9	13	102	52	12	—	14
10	38	102	52	25	—	36
11	51	102	52	25	—	50
12	127	102	52	25	—	126
13	381	102	52	25	—	385
14	508	102	52	25	—	510

The results presented in Table II show that the tin collection of silver is essentially complete and also indicate that in the determination of silver by AAS there are no inter-element interferences over a relatively wide range of silver: precious metal ratios.

Slag loss during crucible fusion

To determine the magnitude of the slag loss directly, two separate charges were each salted with 135 mg of silver. After the crucible fusion operation, the slags were crushed and assayed by the conventional lead collection technique. The resultant lead buttons, weighing approximately 40 g each, were cupeled to give silver beads which were then weighed on a microbalance. The silver recovered from the original assay averaged 0·015% of the silver taken.

Application to silver ores and metallurgical products

To determine its reliability, the proposed method was applied to the analysis of a number of silver-bearing ores and concentrates which had been analysed previously by conventional methods. Table III gives the silver results obtained by the proposed method, and those obtained by methods based on preconcentration by lead collection techniques.

Table III shows that the results obtained by the proposed method are in good agreement with those obtained by conventional methods (including those involving the spectroscopic analysis of assay beads) on a wide variety of materials.

TABLE III.—DETERMINATION OF SILVER IN ORES AND CONCENTRATES

Sample no.	Nature of sample	Sample wt., *assay ton*	Pt	Pd	Rh	Au	Silver found, *troy oz/ton*	
			*troy oz/ton**				Proposed method	Lead collection method
1	Ni-Cu Matte	¼	0·41	0·07	—	0·12	2·56 2·51	
2	Sudbury Concentrate	½	0·11	0·38	0·016	0·017	0·29 0·27	0·25† (5)
3	Tulameen Magnetic Concentrate	½	0·10	—	—	—	0·06 0·06	0·05† (4)
4	South Africa Head Ore	1	0·13	0·06	0·01	0·01	0·019 0·020 0·017 0·025	0·02§ (4)
5	Yellowknife Siliceous Ore	½	—	—	—	—	0·32 0·31	0·32 (2)
6	Yellowknife Siliceous Ore	½	—	—	—	—	1·05 1·02	1·16 (2)
7	Rougher Tail	1	—	—	—	—	0·28 0·30	0·30 (2)
8	Zinc Concentrate	¼	—	—	—	—	16·9$_6$ 16·5$_1$	16·6$_4$ (2)
9	Copper Concentrate	$\frac{1}{5}$	—	—	—	—	75·2$_5$ 75·0$_0$	73·3$_3$ (2)
10	Silver Concentrate	$\frac{1}{5}$	—	—	—	—	126·$_0$ 128·$_0$	130·$_0$ (2)

* Determined by methods described in reference 1.
† Comparison values obtained by independent laboratory by spectrographic method.
§ Comparison values obtained by independent laboratory by atomic absorption.
Figures in parenthesis indicate number of replicate determinations.
Assay tons and troy oz/ton have been used as units although they are not S.I. units; in permitting this usage an exception has been made to the general rule [Ed.].

Samples 1 and 2 require special mention because these materials are rich in both base and platinum-group metals. When the conventional lead-collection method is used on such materials, many scorifications are necessary to produce lead buttons that are free of base metals, even with 0·25-assay-ton samples. The precious metal bead that is obtained by cupellation of these buttons must then be analysed for gold and platinum-group metals before a silver value can be obtained by difference. Obviously, such a scheme is tedious, time-consuming, and subject to errors.

Certain of the larger industrial laboratories determine silver directly in beads containing a mixture of the precious metals, by emission spectroscopy; however, this procedure is not available to most of the smaller commercial laboratories.

Because of the problems noted above, only the silver value obtained by the proposed method is given for sample 1 (Cu–Ni Matte) in Table III.

DISCUSSION

Although the standard method for the determination of silver by fire assay has been used for many years, there are numerous problems associated with the analysis of base and precious metal concentrates for silver. Previous workers have reported slag losses of 0·2 % on a single scorification of impure lead buttons, and a minimum of 2 % cupellation loss.[5,6] Therefore, several scorifications could give total errors of up to 5 % on treatment of buttons rich in base metals.

An additional source of error in the conventional method is associated with the manipulation and weighing of small beads in the analysis of samples low in silver. Therefore, these operations, linked with the problems associated with the presence of gold and platinum-group metals in silver beads as described above, increase the probability of error in the silver value.

Even when applied to complex materials containing base and platinum-group metals (samples 1 and 2, Table III) the proposed method is free from the problems mentioned above. Indeed, all samples listed in Table III were treated by the same relatively simple, rapid and direct procedure. This simplicity is possible because silver can be determined by AAS on a relatively small aliquot of the sample solution, and separation from tin, base metals (mainly copper), gold and platinum-group metals is not necessary. There is the additional advantage that the remaining bulk of the sample solution is available, when necessary, for the determination of other precious metals by the previously described procedures associated with the tin-collection scheme.[1]

Acknowledgement—The authors wish to thank Mr. G. H. Faye for his assistance as technical reviewer of this note.

Zusammenfassung—Ein neues Verfahren zur Bestimmung von Silber in Erzen und metallurgischen Konzentraten wird beschrieben. Das Verfahren beruht auf der Sammlung des Silbers in einem Zinnregulus bei einem Schmelzaufschluß und anschließender Bestimmung durch Atomabsorptions-Spektralphotometrie. Das vorgeschlagene Verfahren geht schnell, ist frei von Störungen durch andere Elemente, und die Ergebnisse halten jedem Vergleich mit auf andere Weise erzielten stand.

Résumé—On décrit une nouvelle méthode de détermination de l'argent dans les minerais et concentrats métallurgiques. La technique est basée sur la collection de l'argent dans un bouton d'étain durant une fusion par voie sèche, et la détermination subséquente par spectrophotométrie d'absorption atomique. La méthode proposée est rapide, exempte d'interférences interéléments, et les résultats obtenus sont en accord favorable avec ceux obtenus par d'autres méthodes.

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U(VI) COMPLEXES OF OXINE AND DERIVATIVES

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Summary—Infrared bands due to the hydrogen-bonded $^{+}N—H\cdots O$ system in the oxine adduct of U(VI) have been identified and found to occur in the spectra of several newly prepared U(VI) adducts of oxine derivatives. Interligand steric effects in the U(VI) complexes of most 7-substituted oxines prevent the formation of the 1:3 adduct. Complexes of the type ML_2X, where X is a small co-ordinating species present in solution, are formed instead. With 2-substituted oxines, steric interactions between the 2-substituent and co-ordinated water result in destabilization of the complex and subsequent hydrolysis as the pH of the solution is raised. Experiments involving the use of [^{14}C]-oxine were found to distinguish between co-ordinated and lattice-held oxine and are potentially valuable in studies of oxine adducts formed by other metal ions.

The red adduct, $UO_2(C_9H_6NO)_2{\cdot}C_9H_7NO$, formed between uranium(VI) and oxine (8-hydroxyquinoline) has been used in chemical analysis for several years.[1] Until recently, there had been some speculation about the manner in which the additional molecule of oxine (HOx) is bound. Suggestions[2,3] that this molecule is an unco-ordinated crystal-lattice component conflicted with those[4–8] that it is co-ordinated to the central uranium(VI) atom. A subsequent X-ray structure determination[9] by Hall *et al.* showed that the extra molecule is indeed co-ordinated to the uranium(VI) atom, but through the phenolate oxygen only. In a recent communication,[10] the present authors reported the location of the acidic proton in the adduct, and a series of new uranium(VI) complexes of HOx derivatives. Also, reference was made to a method involving the use of [^{14}C]-HOx for investigating the nature of the adduct. In the present report we wish to provide the details of the communication and of the findings of more recent work.

EXPERIMENTAL

Chemicals

All common chemicals were of suitable purity for the intended purpose. $UO_2(NO_3)_2{\cdot}6H_2O$ (AnlaR grade, B.D.H.) was used without further purification. Oxine, 2-methyl- and 5-chloro-oxine were obtained commercially and purified by sublimation or recrystallization; 2,7-dimethyloxine was available in the laboratory. [^{14}C]-Oxine was synthesized as described earlier.[11] Its specific activity was 3·6 mV sec^{-1} mg^{-1}.* The following derivatives were synthesized by procedures in the literature: 2-n-butyl,[12] 2-phenyl,[13] 2-(2′-thienyl),[14] 5-methyl,[15] 5-phenyl,[16] 5-acetyl,[17] 5-nitro,[18,19] 7-methyl,[20] and 7-phenyloxine.[16]

7-t-Butyloxine was synthesized by a Skraup-type reaction. 2-Amino-6-t-butylphenol (21 g) and glycerol (72 g) were condensed in concentrated sulphuric acid (22 ml) at 130–140° for 4 hr in the presence of 2-nitro-6-t-butylphenol (15 g) as an oxidant. The viscous reaction mixture was cooled, diluted with water, and the excess of oxidant removed by steam-distillation. After neutralization with sodium hydroxide, the mixture was steam-distilled to give 7-t-butyloxine. The product was purified by further steam-distillation and recrystallization from aqueous ethanol to yield white needles, m.p. 92–93°. The yield was 25%, calculated on the amount of amino compound taken. Calculated for $C_{13}H_{15}NO$: C, 77·58%; H, 7·51%; N, 6·96%. Found: C, 77·5%; H, 7·5%;

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* Measurements of [^{14}C]-activity were made by the "rate of drift" method which yields units of mV sec^{-1} mg^{-1} (see V. F. Raaen and G. A. Ropp, *Anal. Chem.*, 1953, **25**, 174). Conversion into units of disintegrations sec^{-1} mg^{-1} was not necessary.

N, 7·0%. The compound was further characterized by infrared, mass and NMR spectroscopy. All spectra exhibited the expected features. The starting compound, 2-amino-6-t-butylphenol, was prepared by nitration of 2-t-butylphenol,[21] followed by hydrosulphite reduction to the amine.

Synthesis of uranium(VI) complexes

The complexes were precipitated from aqueous solution or from 40% v/v acetone–water solution when ligands of low aqueous solubility were used. The pH was adjusted by hydrolysis of urea, or by addition of aqueous ammonia or dilute sodium hydroxide solution.

Precipitation by urea hydrolysis. $UO_2(Ox)_2 \cdot HOx$ was prepared by the procedure of Moeller and Wilkins.[22] The following procedure was used for the preparation of the uranium(VI) complexes of 5-Me (brick-red), 5-Ph (brick-red), 5-NO_2 (yellow), 5-Ac (brick-red), 7-Me (dark brown) and 7-PhOxH (orange-brown). $UO_2(NO_3)_2 \cdot 6H_2O$ (0·20 mmole) dissolved in 50 ml of water containing 2 drops of concentrated nitric acid was warmed to 70–80° and the appropriate reagent derivative (0·72 mmole, but 1·1 mmole of 5-AcOxH) dissolved in 2 ml of glacial acetic acid was added slowly with stirring. After the addition of urea (5·5 g), the mixture was heated to boiling, placed on a steam-bath for 5 hr, with periodic stirring, and then filtered (hot). The pH of the cooled filtrate was 5·8–6·0. The precipitate was washed once with 90% ethanol and 3 times with hot water and was dried overnight on a water-aspirator and then at 100° for 2 hr.

Precipitation by aqueous ammonia. The adduct of 2-MeOxH was prepared by the procedure of Phillips *et al.*[23] The method for the preparation of the 7-Me (dark brown) and 2,7-diMeOxH (brick-red) complexes was similar to the urea procedure except that the pH was adjusted (to 7) by the drop-wise addition of 4*M* ammonia, and the mixture was not boiled. The 7-t-Bu (red-brown) and 5-ClOxH (orange-brown) complexes were prepared as follows. $UO_2(NO_3)_2 \cdot 6H_2O$ (0·20 mmole) was dissolved in 60 ml of water containing 2 drops of concentrated nitric acid and the solution was warmed to 60°. The reagent (0·72 mmole) dissolved in 40 ml of acetone was added slowly, followed by careful addition of 4*M* ammonia to adjust the pH to 7. The solution was cooled to 40–50°, and the precipitate was then filtered off and washed and dried as above.

Precipitation by dilute sodium hydroxide solution. The 7-Me and 2,7-diMeOxH complexes were precipitated by the previous procedure except that 0·2*M* sodium hydroxide was used in place of 4*M* ammonia.

Thermal conversion into 1:2 *complexes*

The adducts of 2-MeOxH and the 5-substituted derivatives were converted into the corresponding bis (1:2) compounds by heating a few hundred mg of each adduct at 210–225° (oil-bath) for 3–4 hr *in vacuo* (0·13 mbar). The sublimed reagent was collected as a compact deposit in the initial portion of a U-tube immersed in a solid-CO_2 bath. In general, the thermal decomposition products were black. All complexes containing ammonia, water or acetone were also converted into the corresponding 1:2 compounds (black) by the same procedure. Only the products from $UO_2(7\text{-MeOx})_2 \cdot H_2O$ and $UO_2(7\text{-t-BuOx})_2 \cdot OC(CH_3)_2$ were analysed.

TABLE I

Derivative	Formula	Calculated (%)					Found (%)				
		C	H	N	Cl	U	C	H	N	Cl	U
5-MeOxH	$UO_2(C_{10}H_8NO)_2 \cdot C_{10}H_9NO$	48·33	3·38	5·64		31·93	48·4	3·9	5·5		32·0
5-PhOxH	$UO_2(C_{15}H_{10}NO)_2 \cdot C_{15}H_{11}NO$	58·01	3·35	4·51		25·55	57·9	3·4	4·4		25·1
5-NO_2OxH	$UO_2(C_9H_5N_2O_3)_2 \cdot C_9H_6N_2O_3$	38·67	1·93	10·03		28·38	37·6	2·0	10·0		29·1
5-AcOxH	$UO_2(C_{11}H_8NO_2)_2 \cdot C_{11}H_9NO_2$	47·74	3·04	5·06		28·67	48·8	2·9	4·9		27·6
7-PhOxH	$UO_2(C_{15}H_{10}NO)_2 \cdot C_{15}H_{11}NO$	58·01	3·35	4·51		25·55	58·3	3·3	4·6		25·1
7-MeOxH	$UO_2(C_{10}H_8NO)_2 \cdot NH_3$*	39·81	3·17	6·96		39·45	39·6	3·0	6·4		39·4
7-MeOxH	$UO_2(C_{10}H_8NO)_2 \cdot H_2O$	39·74	3·00	4·64		39·38	39·8	3·3	4·8		38·8†
							39·3	3·2	4·6		39·6‡
2,7-diMeOxH	$UO_2(C_{11}H_{10}NO)_2 \cdot H_2O$	41·78	3·51	4·43		37·63	42·5	3·7	4·3		36·1†
							43·2	3·7	4·2		35·0‡
5-ClOxH	$UO_2(C_9H_5NOCl)_2 \cdot C_9H_6NOCl$	40·19	2·00	5·21	13·18	29·50	40·2	1·9	5·2	13·05	29·4
7-t-BuOxH	$UO_2(C_{13}H_{14}NO)_2 \cdot OC(CH_3)_2$	47·81	4·70	3·84		32·67	49·7	4·8	4·3		30·1
7-MeOxH	$UO_2(C_{10}H_8NO)_2$	40·96	2·76	4·78		40·58	40·6	3·0	5·1		41·6
7-t-BuOxH	$UO_2(C_{13}H_{14}NO)_2$	46·57	4·21	4·18		35·50	45·8	4·0	4·5		35·7

* A modified Kjeldahl method gave 2·4% NH_3 (calculated, 2·83%).

† Precipitated by aqueous ammonia.

‡ Precipitated by dilute sodium hydroxide solution.

Infrared spectra

Infrared spectra were recorded with a Beckman IR-5 spectrophotometer. The samples were prepared as mulls in spectrally-pure hexachloro-1,3-butadiene. To obtain suitable intensities of the 2050 and 2650 cm^{-1} adduct bands, approximately 2–3 times the quantity of solid usually employed for mull preparation was used.

Exchange between $UO_2(Ox)_2 \cdot HOx$ *and* [^{14}C]-HOx *in solution*

To 5·0 ml of 1,2-dichloroethane containing 52 mg (0·36 mmole) of [^{14}C]-HOx (specific activity, 3·6 mV sec^{-1} mg^{-1}) were added 126 mg (0·18 mmole) of $UO_2(Ox)_2 \cdot HOx$. A heterogeneous system resulted since the solubility (at 25°) of the adduct in dichloroethane is 2·1 mg/ml. The mixture was maintained at 25° and stirred continuously. At the end of the reaction period, it was quickly filtered (~20 sec) and washed with five 2-ml portions of dichloroethane to remove contaminating [^{14}C]-HOx. The solid was then converted thermally into $UO_2(Ox)_2$ and sublimed HOx,[24] and the specific activity of each component was determined as described previously.[11] The reaction times ranged from 5 min to 3 hr. The 3-hr experiment was repeated with 33 mg (0·047 mmole) of the adduct; all other conditions were unchanged.

Potentiometric titrations

All measurements were made in 50% v/v dioxan–water at 25° and $\mu = 0{\cdot}10$ (sodium perchlorate). The ligand protonation constants (Table II) were determined potentiometrically and calculated by a least-squares fit of the linear equation previously given.[25] Chelate formation constants were determined as described elsewhere.[26] In the solution to be titrated (110 ml), the concentrations of ligand and uranium(VI) were 2·2–3·4 × $10^{-3}M$ and 4·5 × $10^{-4}M$, respectively. For converting pH-meter readings into $-\log [H^+]$, the correction factor $-0{\cdot}08$ was used;[25] p_cK_w was 15·37. The general equations of Hearon and Gilbert were used to calculate $\bar{n}$ and [L] values.[26] Examination of the formation curves for the 2-Me and 2-n-BuOxH-U(VI) systems led to the selection of data points within the narrow ranges $\bar{n}$ = 0·3–0·7 and 0·3–0·6, respectively. Asymmetry in the formation curves above $\bar{n} \sim 0{\cdot}7$ coincided with observed precipitation in the titrations. For titrations involving the 2-phenyl and 2-(2′-thienyl) substituted ligands, values of $\bar{n} > 0{\cdot}2$ could not be obtained, because of precipitation of hydrolysed species. After selection of the primary titration data corresponding to the above $\bar{n}$ ranges quoted, the formation constants were calculated (Table II) with the aid of a CDC6400 computer using the programme SCOGS,[27] which was modified slightly to suit the needs of the present work.

TABLE II.—PROTON AND U(VI) FORMATION CONSTANTS OF 2-SUBSTITUTED OXINES IN 50% AQUEOUS DIOXAN, 25°C

Derivative	Log K_{NH}	Log K_{OH}	Range $\bar{n}$	Log K_1	Log K_2
HOx	4·12	11·12	0·4–1·5	11·42	9·67
2-MeOxH	4·75	11·60	0·3–0·7	10·28	—
2-n-BuOxH	4·58	11·93	0·3–0·6	10·39	—
2-(2′-Th)OxH	1·48*	11·64	—	—	—
2-PhOxH	2·36	11·77	—	—	—
7-t-BuOxH	2·50	13·4†	0·4–1·5	13·4	11·6

* Reference 14.
† Estimated value.

RESULTS AND DISCUSSION

The X-ray studies by Hall, Rae and Waters[9] have shown that the three oxine molecules in $UO_2(Ox)_2 \cdot HOx$ are co-ordinated to the central uranium(VI) atom. Two ligands are bidentate and one is monodentate, being co-ordinated through the oxygen atom only. The three ligands are approximately coplanar about the nearly linear uranyl ion. In view of the interatomic distances and angles, it was suggested that the monodentate ligand is bound as a zwitterion, and that the zwitterion proton is hydrogen-bonded to the oxygen atom of the neighbouring bidentate ligand. This suggestion was proved correct in a subsequent communication[10] in which the present authors showed that the broad 2650 and weak 2050 cm^{-1} bands in the infrared spectrum of the adduct (spectrum A in reference 10) arise from the triatomic system $^{+}N—H \cdots O$. These bands were overlooked in previous investigations but are clearly apparent when an increased amount of the adduct is taken for mull preparation. That the bands are due to a protonic vibration is demonstrated by their absence in the spectrum of the sodium salt (prepared by the procedure of Bullwinkel and Noble[4]), and by the appropriate isotopic frequency shifts in the spectrum of the complex precipitated from D_2O ($\nu_H/\nu_D = 1{\cdot}29$ and $1{\cdot}35$ for the 2650 and 2050 cm^{-1} bands, respectively). The following evidence clearly associates these protonic bands with the $^{+}N—H \cdots O$ system: (*i*) similar bands (but of greater intensity) are observed in the spectra of the hydrochloride salts of HOx and of other derivatives such as 2-MeOxH and 8-methoxyquinoline but are not present in those of the neutral ligands; (*ii*) the bands are similar in appearance and location to the band structure observed for pyridine hydrochloride and other protonated amines.[28–33] The broadness of the 2500 cm^{-1} band in the pyridine hydrochloride spectrum and its displacement from the free $^{+}N—H$ stretching frequency (3200–3400 cm^{-1}) have been shown to be due to the $^{+}N—H \cdots Cl$ hydrogen-bonded system; (*iii*) a molecular model of the adduct, based on the X-ray structure, reveals that the nitrogen proton makes a direct approach to the oxygen atom of the neighbouring bidentate ligand, to which hydrogen-bonding almost certainly must occur. [A strong hydrogen bond, as suggested by the short N—O distance (0·271 mm)[9] would contribute appreciable additional stability to the monodentate ligand.]

The structure of the sodium salt of the adduct would be of considerable interest. Bullwinkel and Noble[4] have proposed that in the complex anion all ligands are bidentate, but an attempt to determine the structure was not successful.[34]

The 2650 and 2050 cm^{-1} bands are of considerable diagnostic value in the characterization of complexes formed between derivatives of HOx and uranium(VI). For example, these bands are observed* in the spectra of the uranium(VI) complexes formed by 2-Me, 5-Me, 5-Cl, 5-Ac, 5-Ph, 5-NO_2 and 7-PhOxH, showing that these compounds are adducts. Typical examples are provided by spectra *A*, *B* and *C*, Fig. 1. Elemental analysis (Table I) confirmed the compositions. The bands are not observed, however, in the spectra of the complexes derived from 7-Me, 2,7-diMe and 7-t-BuOxH, showing that these compounds do not carry the additional zwitterion ligand. Examples are spectra *C* and *D*, Fig. 2. In place of the zwitterion, these compounds contain H_2O, NH_3 or acetone, depending on the conditions of preparation. If the 7-MeOxH complex is precipitated by adjusting the pH with dilute ammonia or sodium hydroxide solution, the composition is $UO_2(7\text{-MeOx})_2{\cdot}H_2O$ (Table I); the band at 3350 cm^{-1} and the broad band centred at ~3000 cm^{-1} in spectrum *D*, Fig. 2, show the presence of water. (A similar hydrate is obtained with 2,7-diMeOxH; the analytical data for this compound strongly suggest the presence of a small amount of reagent contaminant.) Spectrum *E*, Fig. 2, was obtained after the hydrate had been heated *in vacuo* for 3 hr at 210°; the 3350 cm^{-1} band is now absent, the intensity at ~3000 cm^{-1} is reduced, and the composition of the residue is $UO_2(7\text{-MeOx})_2$ (Table I). If the pH is adjusted by urea hydrolysis, the composition is $UO_2(7\text{-MeOx})_2{\cdot}NH_3$ (Table I), and N—H bands are observed in the spectrum (D, Fig. in reference 10) at 3450 and 3300 cm^{-1}. Because of the low solubility of the reagent in water, the

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* In a few instances, the 2050 cm^{-1} band is scarcely discernible.

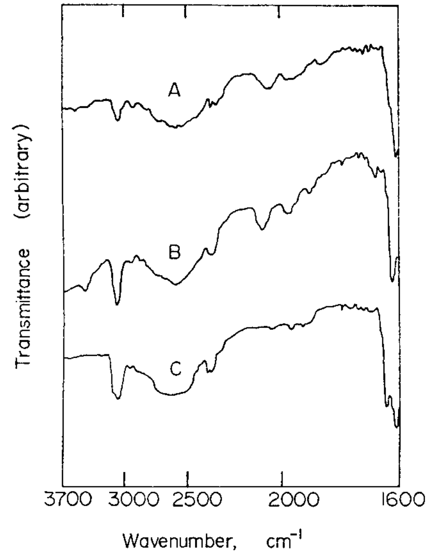

FIG. 1.—Infrared spectra of (*A*) $UO_2(5\text{-}ClOx)_2 \cdot 5\text{-}ClOxH$, (*B*) $UO_2(5\text{-}PhOx)_2 \cdot 5\text{-}PhOxH$, (*C*) $UO_2(7\text{-}PhOx)_2 \cdot 7\text{-}PhOxH$.

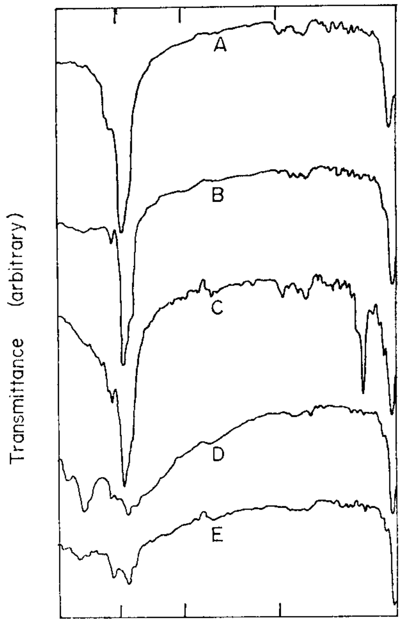

FIG. 2.—Infrared spectra of (*A*) contaminated 7-t-BuOxH complex precipitated from aqueous solution, (*B*) $UO_2(7\text{-}t\text{-}BuOx)_2$, (*C*) $UO_2(7\text{-}t\text{-}BuOx)_2 \cdot OC(CH_3)_2$, (*D*) $UO_2(7\text{-}MeOx)_2 \cdot H_2O$ precipitated with aqueous ammonia, (*E*) $UO_2(7\text{-}MeOx)_2$.

7-t-BuOxH complex was precipitated from an aqueous solution of ~40% v/v acetone–water. The composition of the complex is $UO_2(7\text{-t-BuOx})_2\cdot OC(CH_3)_2$ (Table I); the infrared spectrum (*C*, Fig. 2) clearly shows the stretching frequency of the carbonyl group at ~1690 cm^{-1}. The carbonyl band is not present in spectrum *B*, Fig. 2, which was obtained after the compound had been thermally converted into $UO_2(7\text{-t-BuOx})_2$ (Table I). The value of the 2650 and 2050 cm^{-1} bands as diagnostic aids was well exemplified when the 7-t-BuOxH complex was precipitated from a purely aqueous medium. Elemental analysis showed that the composition of the precipitate was essentially 1:3, but since the spectrum (*A*, Fig. 2) gave no evidence of the $^{+}N—H \cdots O$ band system, it was concluded that the result was fortuitous and due to reagent contamination.*

The thermal conversion of $UO_2(Ox)_2\cdot HOx$ into $UO_2(Ox)_2$ yields a spectrum (C, Fig. in reference 10) in which the $^{+}N—H \cdots O$ bands are absent. Similarly, the bands are not present in the spectra of the products obtained on thermal treatment of the adducts of 2-MeOxH and the 5-substituted oxines. Since elemental analysis of these thermal products was not made, it is only presumed that they are the corresponding 1:2 compounds. In general, these thermal products resemble $UO_2(Ox)_2$ in colour (black).

In the light of the infrared band system of the $^{+}N—H \cdots O$ grouping, it is worth commenting on the compound $[UO_2(Ox)_2]_2\cdot HOx$ first prepared by Bordner *et al.*[35] and later examined by Magee and Gordon[36,37] and Magee and Woodward.[38] It has been suggested[38] that this compound is an amorphous polymer with the basic polymeric unit composed of the 1:3 and 1:2 compounds held together by a bond between the nitrogen atom of the monodentate ligand and the uranium atom of the 1:2 compound. In turn, the basic polymeric units are bonded by a proton bridge between the uranyl oxygens of the 1:2 compound in adjacent units. This suggestion is probably not correct since the reported infrared spectrum[38] of the compound exhibits the $^{+}N—H \cdots O$ band system. Therefore, in $[UO_2(Ox)_2]_2\cdot HOx$, the proton is located on the nitrogen atom, and some form of bonding other than that proposed by Magee and Woodward is required to hold the 1:3 and 1:2 components together in a unit, and to expand the unit polymerically.

The construction of Courtauld molecular models shows that the failure of 7-Me, 2,7-diMe and 7-t-BuOxH to form 1:3 adducts is due to interligand steric repulsions. These repulsions are demonstrated in Fig. 3 for the hypothetical 7-MeOxH adduct. The basic structure reported by Hall *et al.*[9] for the HOx adduct was used as a model. The crosses (7-Me groups) and short lines (α-hydrogen atoms) have been drawn to scale. The heavy dots represent the centres of the hydrogen atoms. The repulsions occur between (*i*) the hydrogen-bonded proton and the 7-Me group of the neighbouring bidentate ligand, (*ii*) the α-hydrogen of the mono-dentate ligand and the 7-Me group of the neighbouring ligand, and (*iii*) the 7-Me group of the monodentate ligand and the α-hydrogen of the neighbouring ligand. As a result of these repulsions, smaller co-ordinating species such as H_2O, NH_3 and acetone replace the monodentate reagent molecule.

The formation of an adduct with 7-PhOxH, although initially surprising, is also explicable on the basis of molecular models. In the ligand, the phenyl group is

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* The contamination is not completely eliminated by use of a 40% acetone solution, as is evidenced by the high result for %C and %N and low result for %U in Table I.

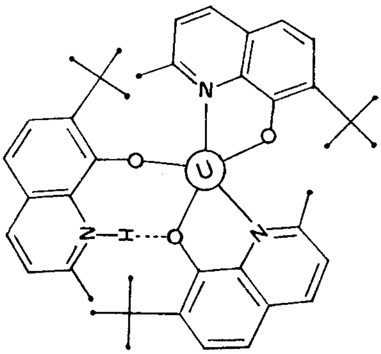

FIG. 3.—Steric interactions in hypothetical U(VI) adduct of 7-MeOxH.

twisted out of the plane of the quinoline ring because of steric hindrance between (*i*) the 6-hydrogen atom (quinoline ring) and the 2′-hydrogen atom (phenyl ring), and (*ii*) the quinoline oxygen atom and the 6′-hydrogen atom. Because of this effect, three such twisted ligands can be arranged equatorially around the uranyl ion and hydrogen-bond formation allowed, provided small deviations from coplanarity around the uranyl-ion are made. An X-ray structure of this compound is required to verify these interactions and would be of considerable interest.

The models also reveal that although considerable crowding exists in the adduct of 2-MeOxH, it is not quite as severe as in the 7-MeOxH adduct, and adduct formation should occur, as is observed. However, it is obvious from the models that substituents of larger size will prevent adduct formation. Thus, attempts to prepare the adduct with 2-n-Bu, 2-Ph and 2-(2′-Th)-OxH failed. Indeed, these ligands did not yield even the ML_2X compounds, as are normally obtained with the 7-substituted oxines. No well-defined chelates were obtained; the precipitate was largely hydrolysed uranium(VI) and precipitated reagent (even in acetone solution).

The failure to precipitate complexes of the type ML_2X is not due to interligand repulsions but to steric interactions between the 2-substituent and one or more water molecules remaining in the co-ordination plane of the uranyl ion. This effect has been previously described for the complexes of 2-substituted oxines and transition-metal ions and results in reduced values of log K_1.[14] In Table II, even though the log K_{NH} and log K_{OH} values for 2-MeOxH and 2-n-BuOxH are larger than the corresponding values for HOx, the log K_1 values are lower by more than one log unit. With 2-(2′-Th)-OxH and 2-PhOxH, the combination of a larger substituent and a greatly reduced log K_{NH} value results in hydrolysis even during addition of the first ligand molecule. Curve *D*, Fig. 4, for the 2PhOxH system shows hydrolysis beginning at ~pH 4; at ~pH 5·7, a significant amount of solid hydrolysis products is present. Values of $\bar{n}$ did not exceed 0·1. The behaviour of the 2-(2′Th)-OxH system was similar ($\bar{n} < 0{\cdot}2$).

With the transition metal-ions, the occurrence of distortion towards a tetrahedral configuration on addition of the first ligand molecule relieves the steric interactions and permits substitution of the second ligand molecule without a serious decrease in stability, such that log $K_2 >$ log K_1.[14] In the present study, hydrolysis prevented the determination of log K_2 values for the 2-MeOxH and 2-n BuOxH systems (Table II;

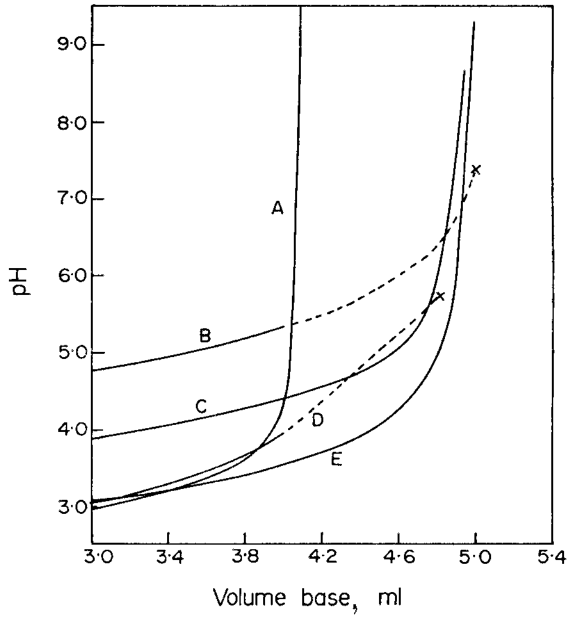

FIG. 4.—Titration curves for (*A*) $HClO_4$, (*B*) $HClO_4$/2-MeOxH/U(VI), (*C*) $HClO_4$/HOx/U(VI), (*D*) $HClO_4$/2-PhOxH/U(VI), (*E*) $HClO_4$/7-t-BuOxH/U(VI) systems. Dashed lines indicate fading of U(VI)-ligand complex colour owing to hydrolysis, and X denotes precipitation of hydrolysis products.

curve *B*, Fig. 4). This result likely arises from the fact that the essentially linear uranyl ion is not readily distorted, thus allowing hydroxyl ion to compete successfully for the remaining co-ordination sites.

Indirect evidence of the steric interactions with co-ordinated water is provided by the 7-t-BuOxH system (Table II; curve *E*, Fig. 4). Because the oxygen donor atom, unlike the nitrogen donor atom, is not heterocyclic, the 7-position is not sterically equivalent to the 2-position and, as suggested by molecular models, interference with co-ordinated water should not occur. This is verified experimentally by the log K_1 and log K_2 values, which are normal in all respects.

Experiments involving exchange of the oxine ligands in $UO_2(Ox)_2{\cdot}HOx$ with [^{14}C]-HOx in dichloroethane showed that the extra reagent molecule is co-ordinated and is not a lattice component. Although, in view of the published X-ray structure,[9] this information is not new, the experiment was deemed important because of its potential application to oxine adducts of other ions for which no X-ray structures are available. It has been previously demonstrated[39] that when $UO_2(Ox)_2$ is placed in contact with a solution of HOx, addition of the extra molecule occurs. When [^{14}C]-HOx is used in place of HOx, the amount of activity found in the addition product (2·0 mV/sec mg), and in the $UO_2(Ox)_2$ (1·9) and sublimed HOx (2·2) obtained on thermal treatment of the addition product, is very high after only a 5-min reaction period. The activity is much higher than expected for the simple addition of [^{14}C]-HOx to $UO_2(Ox)_2$. Therefore, it was concluded that an exchange process involving the inactive ligands of the bis compound and [^{14}C]-HOx in solution occurs concurrently with the addition reaction. In the present work, the experiment was repeated with $UO_2(Ox)_2{\cdot}HOx$ in place of $UO_2(Ox)_2$. For reaction times of 30 min or less, no activity was found in the bis compound and sublimed oxine after thermal conversion of the isolated adduct. After 3 hr, the specific activity was small (~0·1 mV/sec mg). For complete exchange of all three ligands, the specific activity should be 1·4 mV/sec mg. (Since 126 mg of the adduct contain 77 mg of inactive HOx, and 52 mg of [^{14}C]-HOx were dissolved in the dichloroethane, the specific activity after exchange equilibrium is reached should be $[52{\cdot}0/(77{\cdot}3 + 52{\cdot}0)] \times 3{\cdot}6 = 1{\cdot}4$ mV/sec mg.) The small amount of activity found is not consistent with a structure in which the extra reagent molecule is a lattice component for, if this was the structure, the isolated adduct (or its thermal decomposition products) would have been highly radioactive after just a few minutes. This follows because on dissolution, the adduct would dissociate into HOx and $UO_2(Ox)_2$ and as shown previously,[39] the bis compound would undergo exchange and addition, rapidly incorporating [^{14}C]-HOx in the process. The results provide strong evidence, however, that the adduct is dissolved as a molecular entity.

Since solubility equilibrium is achieved in about 5 min, the 3-hr reaction time would appear to be more than adequate for participation in the solubility equilibrium of the total amount of adduct taken. As a precaution, however, the experiment was repeated with 33 rather than 126 mg of adduct. After 3 hr, the specific activity of the isolated adduct and its thermal decomposition products was 0·36 mV/sec mg (2·6 for exchange equilibrium), in accord with the first result.

The main limitation of the test in its application to other adducts is that it probably would not distinguish between a very weakly co-ordinated molecule and a lattice-held molecule.

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Zusammenfassung—Von dem Wasserstoffbrückensystem $^+N—H \ldots O$ herrührende Infrarotbanden wurden im Oxinaddukt von Uran(VI) identifiziert; sie finden sich auch in den Spektren mehrerer neu hergestellter U(VI)-Addukte von Oxinderivaten. Sterische Effekte zwischen den Liganden verhindern bei den Komplexen der meisten 7-substituierten Oxine die Bildung des 1:3-Adduktes. Statt dessen bilden sich Komplexe von Typ ML_2X, wo X eine in der Lösung vorhandene kleine koordinierende Spezies bedeutet. Bei 2-substituierten Oxinen führen sterische Wechselwirkungen zwischen dem 2-Substituenten und dem koordinierten Wasser zu einer Destabilisierung des Komplexes und anschließender Hydrolyse, wenn der pH der Lösung erhöht wird. Experimente mit [^{14}C]-Oxin unterscheiden zwischen koordiniertem und im Gitter gebundenem Oxin und können bei Untersuchungen von Oxinaddukten anderer Metallionen gegebenenfalls nützlich sein.

Résumé—On a identifié des bandes infra-rouges dues au système $^+N—H \ldots O$ à liaison hydrogène dans le complexe de l'oxine avec U(VI) et l'on a trouvé qu'elles apparaissent dans les spectres de plusieurs complexes nouvellement préparés de U(VI) avec des dérivés de l'oxine. Les influences stériques interligand dans les complexes de U(VI) avec la plupart des oxines 7-substituées empêchent la formation du complexe 1:3. Les complexes du type ML_2X, oú X est une petite espèce coordinante présente en solution, sont formés à la place. Avec des oxines 2-substituées, les interactions stériques entre le substituant en 2 et l'eau de coordination ont pour résultat une déstabilisation du complexe et une hydrolyse subséquente quand on élève

le pH de la solution. On a trouvé que des expériences mettant en jeu l'emploi d'oxine (^{14}C) distinguent entre l'oxine coordonnée et celle fixée par le réseau et sont potentiellement interessantes dans des études sur les composés d'addition que forme l'oxine avec d'autres ions métalliques.

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SPECTROPHOTOMETRIC DETERMINATION OF CYANIDE WITH ORGANIC DISULPHIDES

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Summary—The reaction of cyanide ion with the disulphides 2,2′-dithiodipyridine, 4,4′-dithiodipyridine, 2,2′-dithiodipyrimidine, and 5,5′-dithiobis(2-nitrobenzoic acid) to displace an absorbing thiol anion has been evaluated for the spectrophotometric determination of cyanide. Reaction is somewhat slow and is applicable to cyanide determination in the range 0·2–5·0 μg/ml. By variation of reactant ratios and pH the concentration range can be increased to 50 μg/ml. The reaction is faster when cyanide is present at a higher concentration than the disulphide.

ORGANIC disulphides undergo a nucleophilic displacement reaction with cyanide ion to yield a thiol anion and an organic thiocyanate, as shown in equation 1.[1] In some instances desulphurization occurs, yielding a monosulphide and thiocyanate ion. This is believed to result from the further reaction of the thiol anion with the organic thiocyanate to displace the thiocyanate ion.[2] This reaction is shown in Equation 2.

$$\mathrm{RSSR} + \mathrm{CN^-} \rightarrow \mathrm{RS^-} + \mathrm{RSCN} \qquad (1)$$

$$\mathrm{RSCN} + \mathrm{RS^-} \rightarrow \mathrm{RSR} + \mathrm{SCN^-} \qquad (2)$$

Some unsymmetrical disulphides, RSSR′, where R is 2,4-dinitrophenyl and R′ is benzyl, ethyl or phenyl, were reported to react with cyanide ion at equimolar concentrations in aqueous ethanol or aqueous acetone. Reaction was >90% complete in 5 min at 20–30°.[3] A number of similar compounds with only one nitro group on the aromatic ring were found to react to a somewhat lesser extent. Essentially quantitative reaction of *p*-nitrophenyl disulphide with cyanide ion in 10% aqueous ethanol at 20° was indicated in an extensive spectrophotometric study of the reaction of nucleophiles with disulphides and diselenides.[4]

The disulphide 5,5′-dithiobis(2-nitrobenzoic acid), DTNB, commonly called "Ellman's compound", is widely used for the determination of mercaptan groups.[5] The disulphides 2,2′-dithiodipyridine(2-PDS), and 4,4′-dithiodipyridine(4-PDS), have also been reported to be useful for the determination of thiol groups.[6] A number of related disulphides, including 2,2′-dithiodipyrimidine (2-PyDS), were recently evaluated for the spectrophotometric determination of thiol groups.[7] The visible or ultraviolet absorption of the thiol anion produced is measured and related to mercaptan concentration. A somewhat similar reaction has been found to be useful for the spectrophotometric determination of sulphite ion.[8] The displacement of the thiol anion by sulphite occurs rapidly at room temperature.

Analytical methods for the determination of cyanide were reviewed by Bark and Higson.[9] It appears that one of the most widely used spectrophotometric methods for cyanide ion is the König reaction involving the formation of cyanogen chloride or cyanogen bromide, the subsequent reaction of the cyanogen halide with pyridine to form a quaternary salt, followed by formation of the absorbing species on interaction of the pyridinium salt with an aromatic amine. The compound *p*-phenylenediamine has been reported to be the best for this determination.[10] A sensitive spectrophotometric method has also been reported, based on the cyanide-catalysed reduction of *o*-dinitrobenzene with *p*-nitrobenzaldehyde.[11] The reaction of an insoluble ion-association compound, tris(1,10-phenanthroline)iron(II) tri-iodide, with cyanide ion, to release the free iron complex is reported to be useful over the cyanide concentration range of 0–8 μg/ml.[12] A demasking reaction in which cyanide displaces 8-hydroxy-7-iodo-quinoline-5-sulphonic acid from its Pd(II) complex, followed by formation of the Fe(III) complex of the quinolinesulphonic acid, has been used for colorimetric estimation of cyanide.[13] An indirect procedure has been reported in which cyanide prevents the formation of a ternary complex between silver ion, 1,10-phenanthroline and Bromopyrogallol Red.[14] Sensitive and specific fluorescent methods for cyanide ion have also been developed.[15]

EXPERIMENTAL

Reagents

The 5,5′-dithiobis(2-nitrobenzoic acid), 2,2′-dithiodipyridine, and 4,4′-dithiodipyridine were obtained commercially. The 2,2′-dithiodipyrimidine was prepared by oxidation of 2-mercaptopyrimidine with iodine. The compound was recrystallized from ethyl acetate–petroleum ether and melted at 138–39°.[16] All other chemicals used were the best available reagent grade materials.

Solutions

The potassium cyanide stock solutions were either 0·01 or 0·001M, made up in distilled water, and standardized by silver nitrate titration. They were stable for at least 30 days. The pyridine disulphide and pyrimidine disulphide solutions were prepared by dissolving a weighed amount of the compound in 95% ethanol and diluting it to volume in a volumetric flask. The DTNB solutions were prepared by dissolving a weighed amount of the compound in about 5 ml of 95% ethanol and diluting to 50 ml with the pH-6·86 buffer. The pyridine and pyrimidine disulphides reacted slowly with the pH-6·86 buffer solution. The principal buffers used were 0·025M Na_2HPO_4–KH_2PO_4, pH 6·86, which will be referred to as the pH-7 buffer and 0·01M $Na_2B_4O_7$, pH 9·18, which will be called the pH-9 buffer.

Procedure

Measured volumes of the cyanide and disulphide stock solutions were mixed with a measured volume of the buffer and the reaction allowed to proceed. Usually 1·0 ml of the disulphide solution was used with 0·1–1·0 ml of cyanide solution. The disulphide was usually present in excess and the final volume 10 ml. Most of the reactions involving 4-PDS were carried out at pH 9 and the dilution to final volume was made with the pH-7 buffer. The absorption maximum of the 4-thiopyridone shifts considerably to shorter wavelengths with increasing pH values. The pH must be lowered before the absorbance is measured. The other disulphides and thiol anions showed essentially the same absorption at pH 7 or 9.

RESULTS AND DISCUSSION

Absorption spectra

Wavelength maxima and corresponding molar absorptivity values for the disulphides and reduction products are shown in Table I. These values are essentially constant over the pH range 7–9, except for 4-PDS. Maxima for the thiol anions occur at longer wavelengths than those for the disulphides and are usually far enough removed from the disulphide maxima for the interference to be quite small. However, in the case of 2-PyDS, for best results it was necessary to correct for the absorption of the disulphide present. In all quantitative work at low concentrations of cyanide the disulphide was present in excess. Spectra for reaction solutions showed the maximum

TABLE I.—SUMMARY OF SPECTRAL DATA FOR DISULPHIDES AND THIOL ANIONS*

Compound	Disulphide		Thiol anion	
	λ, *nm*	ε, *l.mole*$^{-1}$.*mm*$^{-1}$	λ, *nm*	ε, *l.mole*$^{-1}$.*mm*$^{-1}$
2-PDS	280	$1{\cdot}00 \times 10^3$	340	700
4-PDS	247	$1{\cdot}58 \times 10^3$	324	$2{\cdot}15 \times 10^3$
2-PyDS	238	$1{\cdot}80 \times 10^3$	277	$1{\cdot}60 \times 10^3$
DTNB	325	$1{\cdot}85 \times 10^3$	412	$1{\cdot}55 \times 10^3$

* These values are from the present work. They are in good agreement with literature results reported in reference 6 for 2-PDS and 4-PDS, reference 7 for 2-PyDS, and reference 5 for DTNB.

for the thiol anion and a peak somewhere near the disulphide maximum, which is presumably due to the organic thiocyanate. This is illustrated in Fig. 1 for the DTNB–CN$^-$ reaction. The absorption of the organic thiocyanate does not interfere in the measurement of the thiol anion.

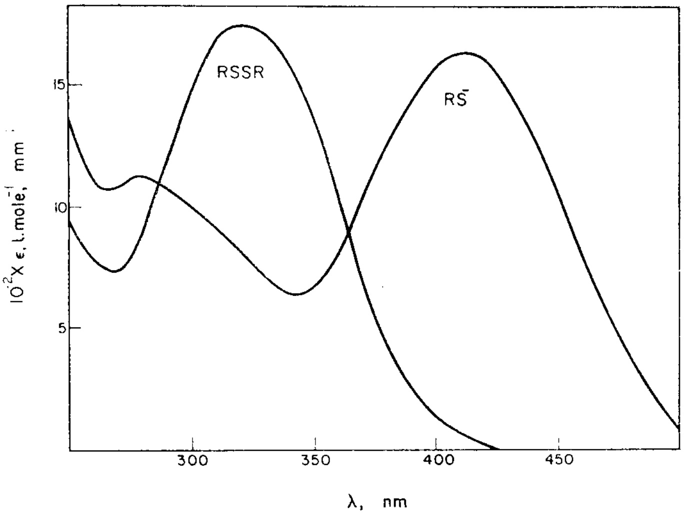

FIG. 1.—Absorption spectra of DTNB and cyanide reaction solution at pH 9.

The absorption of the thiol anion of 4-PDS, 4-thiopyridone, is changed markedly when the pH is increased from 7 to 9. This is shown in Fig. 2. The smaller maximum at 324 nm at pH 9 can be used for analysis but the larger peak at 284 nm is subject to significant interference from tne disulphide. In the work involving 4-PDS and cyanide ion, reactions were carried out at pH 9 and the pH then lowered before absorbance was measured.

Stoichiometry of the reaction

The only course which this reaction takes with these disulphides seems to be that resulting in the displacement of the thiol anion and the formation of the organic thiocyanate. There was no indication of further reaction to form a monosulphide and thiocyanate ion. Continuous-variation and mole-ratio studies indicated a 1:1 reacting ratio for cyanide ion and the disulphides. The extent of reaction of equimolar

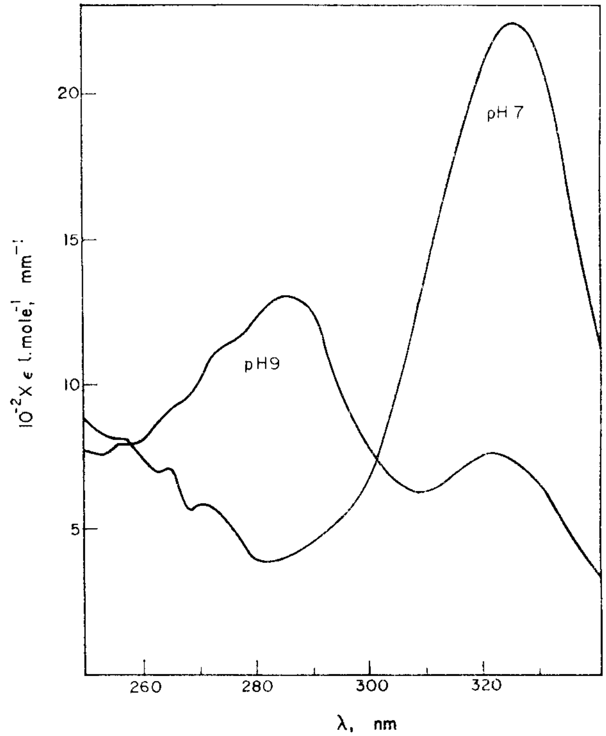

FIG. 2.—Absorption spectra of reaction solutions of 4-PDS and cyanide ion at pH 7 and 9.

concentrations of the reactants is estimated to be about 85% for 4-PDS and 65% for DTNB. These reactions are much less complete than those involving sulphide ion and the same disulphides.[8] A mole-ratio plot for the reaction of cyanide ion and 4-PDS also showed 1:1 stoichiometry. In the case of DTNB the extent of reaction was not high enough for a useful mole-ratio plot to be obtained.

Polarographic studies

Polarograms were obtained of several reaction solutions to show that the disulphide bond is broken in the reaction and that the thiol anion and organic thiocyanate are formed. The compound 4-PDS shows a reduction wave for the disulphide linkage at the dropping mercury electrode, with a half-wave potential, $E_{1/2}$, of −0·45 V *vs.* the saturated calomel electrode (S.C.E.) in a pH-9 buffer. When cyanide ion is present in slight excess, the reduction wave for the disulphide is removed and an oxidation wave appears from 0 to −0·4 V *vs.* S.C.E. This oxidation wave is characteristic of the thiol anion. However, another reduction wave appears in the reaction solution, with $E_{1/2} = -1{\cdot}15$ V *vs.* S.C.E., which is assumed to be due to the organic thiocyanate. Some organic thiocyanates are reported to undergo a two-electron reduction at the dropping mercury electrode, forming the thiol and displacing cyanide ion.[17] Polarography of a solution containing DTNB and a slight excess of cyanide ion also showed the disappearance of the disulphide group and the appearance of an oxidation wave due to the thiol anion. It was not possible to detect with certainty the presence of a wave at more negative potentials, due to the organic thiocyanate, because of the reduction of the nitro group in this region.

Rates of reaction

The reaction of cyanide ion with these disulphides proceeded very slowly when the concentrations of both reactants were about equal, or when the disulphide was present in excess. At pH 9 about 2 hr are required for the reaction to proceed essentially to completion if the concentrations are $<10^{-3}M$, with close to 80% of the reaction taking place within 1 hr. The reaction between cyanide and 2-PyDS seems to be somewhat more rapid than for the other disulphides. It was not possible to speed up the reaction by heating at pH 7 or 9, because the disulphides reacted rapidly with the buffer solutions at elevated temperature. At pH 7 the reaction is too slow to be useful at low concentrations of cyanide with excess of disulphide, while at pH 8 the rate was approximately the same as at pH 9. The solution must be somewhat basic for a reasonable rate of reaction, presumably because the cyanide ion will hydrolyse considerably in water or combine with hydrogen ion at low pH values. The HCN formed will not react with disulphides to displace the thiol. No reaction was evident between DTNB and cyanide ion at room temperature or on heating to the boiling point in solutions made up in distilled water with no buffer present. Some reaction occurred between cyanide and 2-PyDS or 4-PDS in unbuffered aqueous solution but the results were not nearly as good as those obtained at pH 9. For the disulphides used in this study we did not find the speed or completeness of reaction with cyanide ion in unbuffered solutions to be as reported for other disulphides.[3,4] The conversion of disulphide into thiol anion was quite rapid at pH 9 when the cyanide was present in excess. At higher concentrations of cyanide, with the ratio of cyanide to disulphide in the range 2–5 and the disulphide about $10^{-4}M$, the absorbance reaches 0·3–1·0 within 5 min at pH 9 or in 45 min at pH 7.

Determination of cyanide in the range 0·1–5·0 µg/ml

Beer's law data for low concentrations of cyanide are presented in Table II. There appeared to be no significant differences in reaction rate at pH 9 for any of the disulphides, so the compound chosen would depend on the cyanide concentration to be determined. As shown in Table II, 4-PDS offers the highest sensitivity. The disadvantage of this compound is that the pH must be lowered before absorbance measurement. If the measurement is made at pH 9 the sensitivity is lowered considerably. Although 2-PyDS also shows a high sensitivity, the rather high blank due

TABLE II.—BEER'S LAW DATA FOR LOW CONCENTRATIONS OF CYANIDE

CN^-, *µg/ml*	4-PDS		2PyDS		DTNB		2-PDS	
	A, 324 nm	ε*	*A*, 270 nm	ε*	*A*, 412 nm	ε*	*A*, 340 nm	ε*
0·26	0·18	$1{\cdot}80 \times 10^3$	0·14	$1{\cdot}40 \times 10^3$				
0·78	0·51	$1{\cdot}70 \times 10^3$	0·45	$1{\cdot}50 \times 10^3$	0·33	$1{\cdot}10 \times 10^3$	0·21	700
1·30	0·99	$2{\cdot}00 \times 10^3$	0·78	$1{\cdot}56 \times 10^3$	0·56	$1{\cdot}12 \times 10^3$	0·35	700
2·34					0·97	$1{\cdot}08 \times 10^3$	0·62	690
3·12							0·82	680

* Effective molar absorptivity ($l.mole^{-1}.mm^{-1}$) based on cyanide concentration. The disulphide was present in excess. Values are for pH 9 except for 4-PDS which was measured at pH 7.

to absorption of unreacted disulphide is a disadvantage. The compound DTNB is the only one for which the reaction product absorbs in the visible region and so the progress of the reaction can be followed visually. This disulphide is somewhat lower in sensitivity, but also has a lower blank than 4-PDS. As shown in Table II, all the reaction solutions follow Beer's law quite well. The solutions are quite stable, although there is a small increase in absorbance after 2 hr. For best results, measurements should probably be made at a set time after preparation of the solutions.

Recovery data for a limited number of concentrations of cyanide are shown in Table III. Accuracy is reasonably good for these simple synthetic samples.

TABLE III.—RECOVERY DATA FOR SOME SYNTHETIC SAMPLES

CN⁻ present, *μg/ml*	CN⁻ found, *μg/ml*	
	4-PDS*	DTNB
0·26	0·28	
0·78	0·76	0·82
1·30	1·29	
1·56		1·58
2·60		2·60

* Absorbance for 4-PDS solutions measured at 324 nm and pH 7. Absorbance for DTNB measured at 412 nm and pH 9.

Determination of higher concentrations of cyanide with DTNB

Rapid reaction occurs between DTNB and cyanide ion at pH 9 when cyanide is present in excess (mole-ratio of cyanide to DTNB in the range 2–5). Since the absorption increases somewhat rapidly with time, it is important to make measurements at some fixed time after mixing the reactants. The effective molar absorptivity for cyanide on reacting with DTNB for 5 min at pH 9 is 145 $l.mole^{-1}.mm^{-1}$. This can be lowered or raised by decreasing or increasing the reaction time. For example, after 10 min at pH 9 the effective molar absorptivity for cyanide is approximately 250. Beer's law is obeyed under these conditions. The reaction is useful for considerably higher concentrations if the pH-7 buffer is used. The effective molar absorptivity for cyanide after 45 min at pH 7 is 48·0 $l.mole^{-1}.mm^{-1}$ and Beer's law is obeyed. The reaction is much slower at pH 7 so the time of measurement is not quite as critical as at pH 9. It seems likely that the pH, concentration ratio, and reaction time could be adjusted so that a very wide range of cyanide concentrations could be determined.

Interferences

Other substances which would interfere seriously with the determination of cyanide are mercaptans, sulphide and sulphite. It seems possible that some of these interferences could be minimized, since these substances react much more rapidly at a pH $\leqslant 7$ than does cyanide. Preliminary work indicates that sulphide ion reacts with these disulphides with no buffer present, while the reaction with sulphite requires that the pH be in the range 6–9. Conditions could probably be worked out for the determination of cyanide in the presence of such interferences.

The effect of the presence of a limited number of metal ions on the cyanide–disulphide reaction was also investigated. The metal ions were present at a level of 20 μg/ml while the cyanide concentration was 1·0 μg/ml. All the metal ions tested, including Cd, Cu(II), Fe(II), Hg(II), Ni, Pb and Zn interfered seriously, but if EDTA was present (approximately 0·001*M*), Cu(II) and Hg(II) were the only ions which interfered. A pH 9 buffer was used in the interference studies, with a reaction time of 2 hr.

CONCLUSIONS

The determination of cyanide ion with these disulphides is uncomplicated, involving only the addition of the cyanide solution to the disulphide solution and use of the proper buffer. The sensitivity is high and varies with the disulphide used, so it is possible to choose the disulphide which would be most suitable for a given level of cyanide. Also, by choice of pH and disulphide concentration the method can be extended to much higher amounts of cyanide. Because of these factors the method would seem to have a certain amount of versatility. The disadvantage which might be of some importance is the slowness of the reaction with low concentrations of cyanide. The possible interference of certain anions might be significant but it seems likely that a procedure could be worked out to circumvent or minimize these problems.

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Zusammenfassung—Die Reaktion von Cyanidionen mit den Disulfiden 2,2′-Dithiopyridin, 4,4′-Dithiopyridin, 2,2′-Dithiopyrimidin und 5,5′-Dithiobis(2-nitrobenzoesäure) zur Verdrängung eines absorbierenden Thiolanions wurde für die spektrophotometrische Bestimmung von Cyanid verfolgt. Die Reaktion geht verhältnismaßig langsam und laßt sich zur Cyanidbestimmung im Bereich 0,2–5,0 μg/ml verwenden. Durch Änderung der Verhältnisse der Reaktanten und des pH kann man den Konzentrationsbereich bis 50 μg/ml erweitern. Die Reaktion geht schneller, wenn Cyanid in höherer Konzentration vorliegt als das Disulfid.

Résumé—La réaction de l'ion cyanure avec les disulfures 2,2′-dithiopyridine, 4,4′-dithiopyridine et 2,2′-dithiopyrimidine, et l'acide 5,5′-dithiobis-(2-nitrobenzoïque), pour déplacer un anion thiol absorbant, a été évaluée pour la détermination spectrophotométrique du cyanure. La réaction est quelque peu lente et est applicable au dosage du cyanure dans le domaine 0,2–5,0 μg/ml. En faisant varier les rapports de réactifs et le pH, le domaine de concentrations peut être élevé à 50 μg/ml. La réaction est plus rapide lorsque le cyanure est présent à une concentration plus élevée que le disulfure.

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INFRARED DETERMINATION OF BARIUM, STRONTIUM, SODIUM AND POTASSIUM SULPHATES BY THE PELLET TECHNIQUE

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Summary—Methods are proposed for the infrared determination of barium, strontium, sodium and potassium sulphates by the pellet technique. The semimicro sample is mixed with 300 mg of potassium bromide, the pellet is formed, and the peak heights are determined at the appropriate peak. Barium and strontium sulphates are measured at 983 and 993 cm^{-1}, respectively. Sodium and potassium sulphates are both measured at 619 cm^{-1}. Barium and strontium sulphates can be determined in the presence of each other in ratios from 1:20 to 20:1 from the measurements at 983 and 993 cm^{-1}. Carbonates or nitrates do not interfere with any of the procedures.

LITTLE has appeared in the literature on the determination of inorganic sulphates by infrared spectroscopy. Tai and Underwood[1] developed a method for the determination of total sulphate ion by combining freeze drying with the potassium bromide technique. The method involves addition of potassium bromide to an aqueous solution of the sample, shell freezing with a mixture of acetone and solid carbon dioxide, evacuation overnight with a vacuum pump, and formation of the pellet. The method was subsequently applied[2,3] to the determination of sulphate in water and reagent chemicals after use of an ion-exchange colume to remove interferences. The method used the peak at approximately 1130 cm^{-1} and the optimal range was 30–80 μg of sulphate ion. A disadvantage of the method is that it is time-consuming and requires special apparatus. Also, it is so sensitive that it cannot be readily applied to many analytical problems. Underwood, Miller and Howe[4] determined sulphate in aqueous solutions, using an Irtran-2 cell. The sulphate peak at approximately 1130 cm^{-1} was used and the optimal range was 10–50 mg/ml. A disadvantage of this method is that it is lacking in sensitivity and selectivity.

Recently we have proposed a procedure for the determination of inorganic nitrates (barium, strontium, sodium and potassium), alone or in binary mixtures, by the pellet technique.[5] In the present paper the pellet technique is applied to the determination of inorganic sulphates (barium, strontium, sodium, and potassium).

EXPERIMENTAL

Apparatus and reagents

Perkin–Elmer Model 621 infrared spectrophotometer (or equivalent high-precision instrument with scale-expansion facility).

Mechanical vibrating mill (*e.g.*, Wig-L-Bug, Crescent Dental Manufacturing Co., Chicago, Ill.).

Potassium bromide die (*e.g.*, Model 186-0025, Perkin–Elmer Corp.), suitable for vacuum work.

Adapter for mounting KBr disks on spectrophotometer.

Hydraulic press (20 ton; 20 Mg).

Mortars (50 mm) and pestles.

Anhydrous barium, strontium, sodium and potassium sulphates, reagent grade, dried at 110° for 1 hr.

Potassium bromide, infrared grade.

Procedures

Barium sulphate. Prepare 6 disks covering the range 0·1–1·4 mg of barium sulphate, as follows. Weigh the barium sulphate into the mortar to 0·01 mg. Weigh 300 mg of potassium bromide and add it to the mortar in four increasing portions, grinding well after each addition. The total grinding should be time less than 7 min. When the grinding is completed, brush any powder adhering to the pestle back into the mortar. Scrape the mix loose from the mortar and transfer it quantitatively to the die. Level the sample, insert the plunger, evacuate the die for 5 min with a vacuum pump without applying pressure, then apply 8000 kg pressure with a hydraulic press for 7 min.

Dismantle the die and push out the potassium bromide disk by gentle application of the hydraulic press. Mount the disk immediately on an adapter and record the spectrum from 1020 to 820 cm^{-1} using 4x abscissa expansion. (The following settings were used on the Perkin–Elmer model 621 infrared spectrophotometer: slit programme, 1000; gain, 5·1; attenuator speed, 1100; scan drive, 10; scan time, 20; suppression, 0; source current, 0·8).

Determine the absorbance of the peak at 983 cm^{-1} and plot absorbance *vs.* mg of barium sulphate present.

For samples, weigh 0·9–1·4 mg to 0·01 mg, prepare the disk, measure the absorbance at 983 cm^{-1} as just described, and read the amount of barium sulphate from the calibration curve.

Strontium sulphate. Proceed as for barium sulphate but use the peak at 993 cm^{-1}.

Sodium or potassium sulphate. Proceed as before, but calibrate over the range 0·1–1·0 mg of sodium or potassium sulphate. Scan from 820 to 600 cm^{-1} and use the peak at 619 cm^{-1}. Use a 0·7–1·0 mg sample.

Barium and strontium sulphates together. With the vibrating mill prepare seven standard mixtures containing approximately the following amounts of sulphates weighed to 0·1 mg.

No.	1	2	3	4	5	6	7
$BaSO_4$, g	0·90	0·60	0·40	0·30	0·20	0·20	0·10
$SrSO_4$, g	0·10	0·20	0·20	0·30	0·40	0·60	0·90

Weigh 0·9–1·4 mg of each to 0·01 mg and proceed as described for calibration for barium sulphate. Record the spectrum from 1020 to 820 cm^{-1}. Use the absorbance of the peak at 983 cm^{-1} for barium sulphate and at 993 cm^{-1} for strontium sulphate.

Weigh 0·9–1·4 mg of sample, prepare the disk, measure the absorbances at 983 and 993 cm^{-1}, and read the amounts of barium and strontium sulphates from the calibration curves.

DISCUSSION AND RESULTS

Infrared spectra

The infrared spectra of inorganic sulphates have already been described.[6–13] Free sulphate ion has tetrahedral symmetry and should have the four fundamental frequencies reported by Hertzberg[14] (Table I). Most sulphates show variations from these calculated frequencies and the forbidden ν_1 frequency is invariably present in their solid-state infrared spectra.

TABLE I.—FUNDAMENTAL VIBRATIONS OF THE SULPHATE ION.[14]

Type	ν_1	ν_2	ν_3	ν_4
Species	A_1	E	F_2	F_2
Activity	Raman	Raman	I.r. Raman	I.r. Raman
Frequency, *cm^{-1}*	981	451	1104	613
Assignment	Symmetric stretching	Bending deformation (doubly degenerate)	Asymmetric stretch (triply degenerate)	Bending deformtion (triply degenerate)

Hezel and Ross[8,12] considered three possible reasons for the lowering of symmetry in solid sulphates: (*a*) distortion of the SO_4^{2-} tetrahedron in the crystal lattice; (*b*) covalent bonding of the sulphate to the metal through one or more oxygen atoms; (*c*) a non-uniform field due to water molecules around the cation.

The four sulphates dealt with in this report all belong to the space group D_{2h}^{16} with the sulphate ions on C_s sites. The C_s sites provide for up to nine internal vibrations as opposed to the two infrared-allowed fundamental frequencies shown in Table I. The ν_1 and ν_2 vibrations become infrared-allowed and the degeneracies are removed from ν_2, ν_3 and ν_4. Only seven of the nine permitted vibrations have been observed.

The spectra obtained are shown in Figs. 1–4. A suitable peak measurement, the ν_1 vibration, is observed at 983 cm^{-1} for $BaSO_4$ and at 993 cm^{-1} for $SrSO_4$. For Na_2SO_4 and K_2SO_4, a suitable peak, the ν_4 vibration, is observed at 619 cm^{-1}.

Determination of single sulphates

Barium and strontium nitrates and barium and strontium carbonates did not show significant absorption between 1000 and 980 cm^{-1} and should therefore not interfere. Reasonable results (maximum error ~4%) were obtained for the determination of as little as 10% barium or strontium sulphate in the presence of 90% barium or strontium nitrates or carbonates.

Sodium and potassium nitrates did not show significant absorption between 800 and 600 cm^{-1}, and also should not interfere. Reasonable results (maximum error ~9%) were obtained for the determination of as little as 10% sodium or potassium sulphate in the presence of 90% of the nitrate. For lower concentrations for all four sulphates the major absorption band at approximately 1130 cm^{-1} might be used.

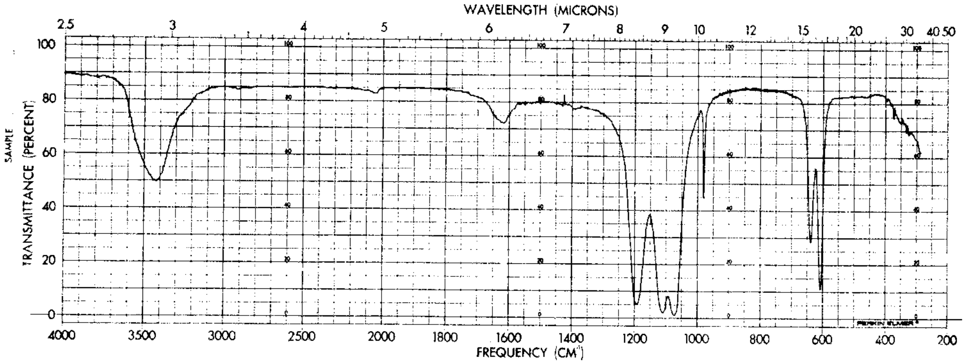

FIG. 1.—Spectrum of $BaSO_4$.

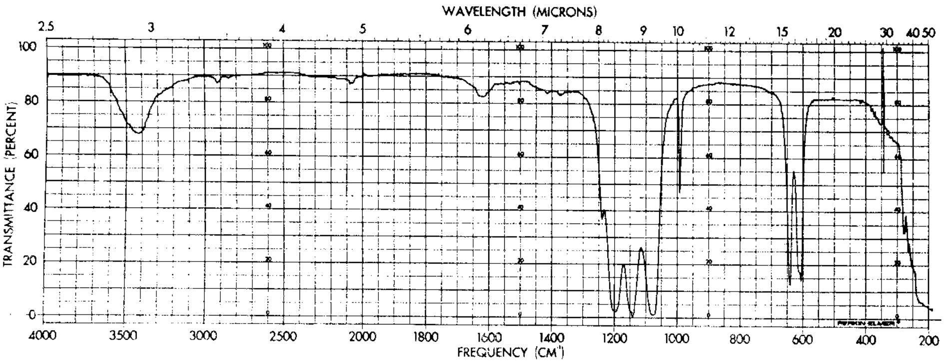

FIG. 2.—Spectrum of $SrSO_4$.

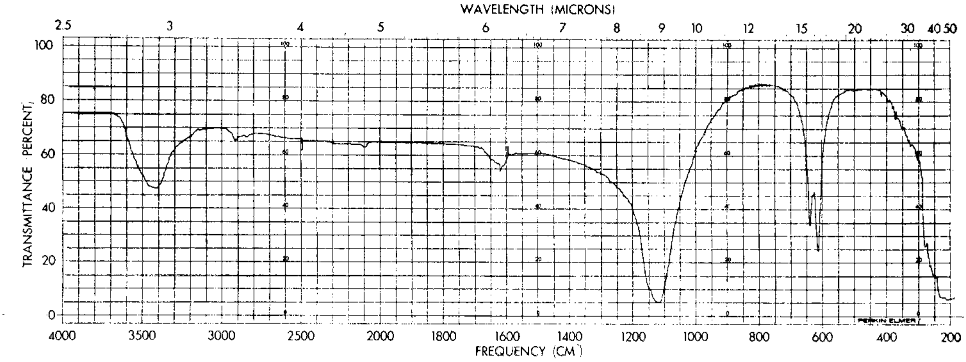

FIG. 3.—Spectrum of Na_2SO_4.

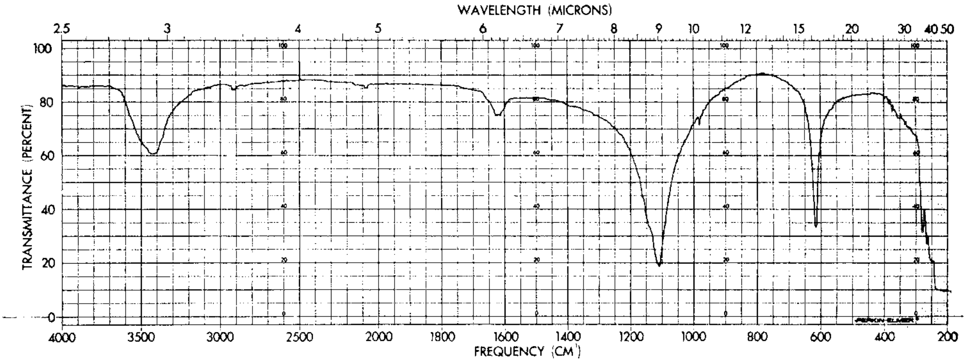

FIG. 4.—Spectrum of K_2SO_4.

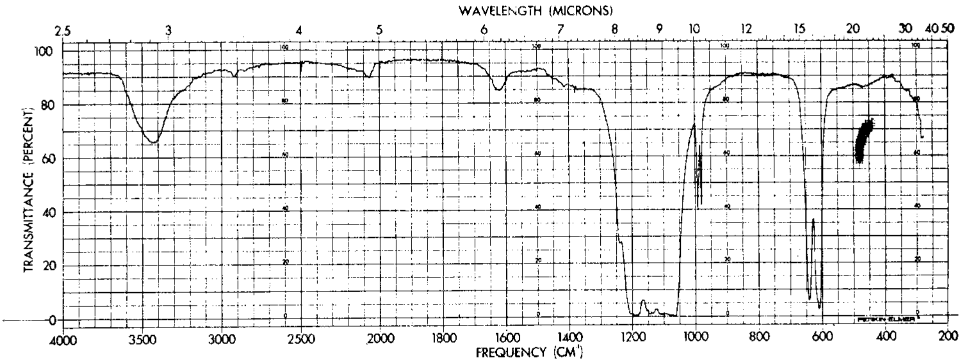

FIG. 5.—Spectrum of $BaSO_4$ plus $SrSO_4$ (1:1).

TABLE II.—RESULTS FOR BARIUM AND STRONTIUM SULPHATE MIXTURES

Added, *mg*				Found, *mg*	
$BaSO_4$	$SrSO_4$	$Ba(NO_3)_2$	$Sr(NO_3)_2$	$BaSO_4$	$SrSO_4$
0·04	1·20			0·02	1·22
0·04	1·22			0·06	1·23
0·04	1·14			0·03	1·13
0·14	1·22			0·17	1·19
0·13	1·10			0·17	1·13
0·15	1·29			0·18	1·26
0·47	0·89			0·47	0·88
0·50	0·96			0·51	0·93
0·51	0·98			0·55	0·97
0·88	0·44			0·88	0·46
0·98	0·49			0·97	0·51
0·87	0·44			0·85	0·44
1·12	0·13			1·13	0·15
1·20	0·14			1·19	0·14
1·30	0·15			1·28	0·17
1·31	0·04			1·32	0·05
1·08	0·03			1·02	0·04
1·35	0·04			1·39	0·04
0·31	0·29	0·29	0·29	0·30	0·26
0·34	0·32	0·33	0·33	0·37	0·33
0·32	0·30	0·32	0·31	0·31	0·27
0·42	0·44	0·20	0·20	0·43	0·44
0·43	0·44	0·21	0·20	0·45	0·45
0·42	0·43	0·20	0·19	0·40	0·40

It was found that the sulphates could not be determined in the presence of sodium or potassium carbonates by the pellet technique, because the hygroscopicity of the latter two salts caused foggy pellets and erratic results.

Analysis of mixtures of sulphates

The spectrum of 1·9 mg of a 1:1 mixture of barium and strontium sulphates is shown in Fig. 5. It is seen that the ν_1 peaks seem suitable for the analysis of the mixture. The method can be used for the range of ratios from 20:1 to 1:20. Outside this range the errors are rather large. The results obtained for mixtures of barium and strontium sulphates are shown in Table II.

The analysis of sodium and potassium sulphate mixtures is not possible because the spectra are too similar.

Zusammenfassung—Methoden zur Infrarot-Bestimmung der Sulfate von Barium, Strontium, Natrium und Kalium nach dem Preßling-Verfahren werden vorgeschlagen. Die Halbmikro-Probe wird mit 300 mg Kaliumbromid gemischt, der Preßling hergestellt und die Höhe der entsprechenden Bande bestimmt. Barium- und Strontiumsulfat werden bei 983 bzw. 993 cm^{-1} gemessen, Natrium- und Kaliumsulfat beide bei 619 cm^{-1}. Barium- und Strontiumsulfat können nebeneinander im Verhältnis 20:1 bis 1:20 aus den Messungen bei 983 und 993 cm^{-1} bestimmt werden. Carbonate und Nitrate stören bei keiner dieser Arbeitsvorschriften.

Résumé—On propose des méthodes pour la détermination infrarouge des sulfates de baryum, strontium, sodium et potassium par la technique de la pastille. On mélange l'échantillon semi-micro avec 300 mg de bromure de potassium, on forme la pastille et les hauteurs de pic sont déterminées sur le pic approprié. Les sulfates de baryum et de strontium sont mesurés à 983 et 993 cm^{-1}, respectivement. Les sulfates de sodium et de potassium sont tous deux mesurés à 619 cm^{-1}. On peut déterminer les sulfates de baryum et de strontium en la présence l'un de l'autre dans des rapports de 1:20 à 20:1 des mesures à 983 et 993 cm^{-1}. Les carbonates ou les nitrates n'interfèrent avec aucune des techniques.

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COULOMETRIC DETERMINATION OF Ce(III) IN ALKALINE SOLUTIONS WITH ELECTROGENERATED OCTACYANOMOLYBDATE(V)

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Summary—The coulometric determination of Ce(III) with octacyanomolybdate(V) in concentrated carbonate–bicarbonate buffer solutions was carried out. The current efficiency for electrogeneration of octacyanomolybdate(V) and the optimum conditions for analytical determinations of microquantities of cerium have been investigated.

The coulometric determination of micro quantities of cerium has been the subject of several investigations. In all of them, owing to the pronounced acid character of Ce(IV) and Ce(III) cations, the analytical methods proposed have been applied exclusively in strongly acid media with electrogenerated reagents such as Fe(II),[1,2] U(IV),[3] Ti(III),[4] Sn(II),[5,6] Mo(V)[7,8] and Ag(II).[9,10]

In the work described in this paper the coulometric–potentiometric determination in alkaline media of micro quantities of Ce(III) with octacyanomolybdate(V) has been studied in detail. First we present the optimum conditions for obtaining quantitative current efficiency in the electrogeneration of the oxidizing agent and subsequently the effect of various factors that affect the determination, *e.g.*, the nature of the supporting electrolyte, temperature, octacyanomolybdate(IV) concentration, Ce(IV) and Ce(III) concentrations that can be estimated.

Because of the easy oxidation of Ce(III) in alkaline solutions and the photodecomposition of octacyanomolybdate(V), the work was done with an inert atmosphere and protection from sunlight.

The current-efficiency study was made according to the method proposed by Lingane,[11] by comparing current-potential curves of the generating electrolyte and the supporting electrolyte alone. The electrolytes used were potassium carbonate solutions and concentrated buffer solutions of potassium carbonate–bicarbonate, which, at the same time as promoting the solubility of cerium ions by complexation, lower the redox potential of the system.[12]

EXPERIMENTAL

Reagents

Potassium octacyanomolybdate(IV) dihydrate. Prepared and purified according to the method of Willard and Thielke.[13]

Cerium(III) solutions. Approximately 0·1 and 0·05*M* solutions were prepared by dissolution of the sulphate monohydrate in 0·05*N* sulphuric acid, and standardized according to the method of Willard and Young.[14]

Potassium carbonate and potassium bicarbonate solutions. Solutions that were 5·5*M* and 2·0*M* respectively were prepared by dissolution of the analytical grade anhydrous salts.

Apparatus

A Metrohm E-211 coulometer was used as the constant current source, and the current-potential curves were obtained by means of a Beckman Electroscan 30. The equivalence point in the coulometric determination was determined by means of a Radiometer pH meter 22 with platinum and

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calomel (S.C.E.) electrodes. Sheets of platinum (surface area 170 mm^2) were used as working and auxiliary electrodes. The auxiliary electrode was kept in a separate cell and electrical connection was made through an agar–potassium chloride plug. A Metrohm EA-876-20 cell (50 ml capacity and equipped for constant temperature) was painted black to exclude light. The solutions were stirred magnetically.

Procedure

Current efficiency for electrogeneration of octaynomolybdate(V). Into the cathode compartment of the electrolytic cell equipped with working, auxiliary and reference electrodes, were introduced 2 ml of 0·1*M* potassium hydroxide, and in the anode compartment 20 ml of supporting electrolyte (carbonate or carbonate–bicarbonate solutions). The temperature of the cell was adjusted to the desired value, with a precision of ±0·1°, and the solution was constantly stirred. By means of an Electroscan 30 in the potentiostat mode, the potential of the working electrode was shifted from 0·4 to 1·2 V at 2 mV/sec. The current in the study of the effect of the supporting electrolyte was adjusted at 2·8 mA and at 7·0 mA when the effect of temperature was determined.

Once the current-potential curve of the supporting electrolyte alone had been determined, 0·075 g of potassium octacyanomolybdate(IV) was introduced into the cell and then the current-potential curve of the complex was obtained under identical conditions.

Coulometric determination of cerium. Changing in each case the variable studied, the following procedure was applied. Into the anode compartment of the cell provided with working, auxiliary, reference and indicator electrodes, 20 ml of supporting electrolyte and 0·075 g of potassium octacyanomolybdate(IV) were introduced and in the cathode compartment 3 ml of 0·1*M* potassium hydroxide. The cell was deaerated with nitrogen or argon of high purity (99·99%) for 5 min, with stirring of the solution. Then a small amount of Ce(III) was added and the pretitration was made, electrogeneration of the oxidizing reagent being continued until the potential of the solution reached 450–500 mV, near the equivalence point; at this moment, the electrolysis was interrupted and a known sample of cerium was added and determined, the determination being regarded as finished when a potential equal to that at the end of the pretitration was attained.

The electrolysis current used was 3 mA in the determination of 6–9 μmole of cerium and 0·3 or 1·0 mA for lower concentrations.

The sample was added by means of a dropper weighed before and after each addition.

RESULTS AND DISCUSSION

Current efficiency

Figures 1 and 2 present some of the current–voltage and current-efficiency curves obtained for the potassium carbonate solutions and the concentrated potassium carbonate–bicarbonate buffer solutions. It is evident that in the majority of the cases studied, the current efficiency obtained was practically quantitative (99·0–100%) when the current density reached was 25 μA/mm^2 or less, except for the analysis done in the carbonate–bicarbonate buffer solution with molar ratio 4·6/0·3. In this instance the low current efficiency was attributed to the reduced diffusion current of the octacyanomolybdate(IV), which in turn was due to the low solubility of the potassium salt in these conditions. As can be seen in Figs. 1 and 2, there is no appreciable difference in the curves obtained under these different conditions, especially among those obtained for the buffer solutions.

Fundamentally, the quantitative current efficiency achieved was possible because of the lack of interference between the residual current due to the water and that which corresponds to the electro-oxidation of the octacyanomolybdate(IV), even though the alkalinity of the supporting electrolyte is increased considerably. A similar study with 0·1 or 0·5*M* sodium hydroxide gave similar results.[15] It must be remembered that in these alkaline media the current efficiency was obtained by comparing directly the experimental current–voltage curves of the generating electrolyte with those of the supporting electrolyte. No correction was made for the possibility that the hydroxyl ions can react chemically with the electrogenerated octacyanomolybdate(V), *via* equation (1):

$$Mo(CN)_8^{3-} + 2\,OH^- \rightleftarrows 1/2O_2 + H_2O + Mo(CN)_8^{4-} \qquad (1)$$

in which case, the effective yield would tend to diminish as the alkalinity increased.

The same level of current efficiency (99·0–100·0%) could be expected for current densities greater than 25 μA/mm^2, so long as the octacyanomolybdate(IV) concentration were increased conveniently. This would be possible because the decomposition potential on the corresponding current–voltage curve will be displaced towards less positive values as the concentration of the complex is increased, thus making more improbable the interference due to oxidation of the water.

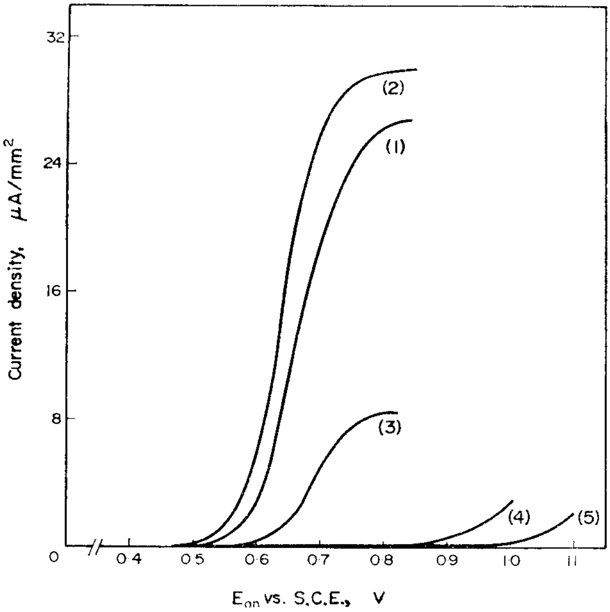

FIG. 1.—Current-anode potential curves for oxidation of octacyanomolybdate(IV). Effect of supporting electrolyte.

(1) In 0·75 or 1·25*M* potassium carbonate. (2) In potassium carbonate–bicarbonate buffer solutions, molar ratio 0·2/1·5 or 1·3/1·3. (3) In potassium carbonate–bicarbonate buffer solution, molar ratio 4·6/0·3. (4), (5) Supporting electrolyte alone, potassium carbonate and potassium carbonate–bicarbonate buffer solutions, respectively.

Coulometric determination of Ce(III)

Effect of the supporting electrolyte. By means of preliminary tests it was found that the level of alkalinity (3*M* potassium carbonate) used in the volumetric determination of Ce(III) with octacyanomolybdate(V)[16] was not applicable to the coulometric determination, even though a current efficiency of 99·0–100% should be expected under such conditions. Nevertheless, the results obtained, with errors up to +100%, and a notable instability of the equivalence potential, in the presence of a slight excess of octacyanomolybdate(V), led us to believe that the reaction (1) takes place preferentially instead of the reaction (2):

$$Mo(CN)_8^{3-} + \text{Ce(III)-carbonate} \rightleftarrows Mo(CN)_8^{4-} + \text{Ce(IV)-carbonate} \qquad (2)$$

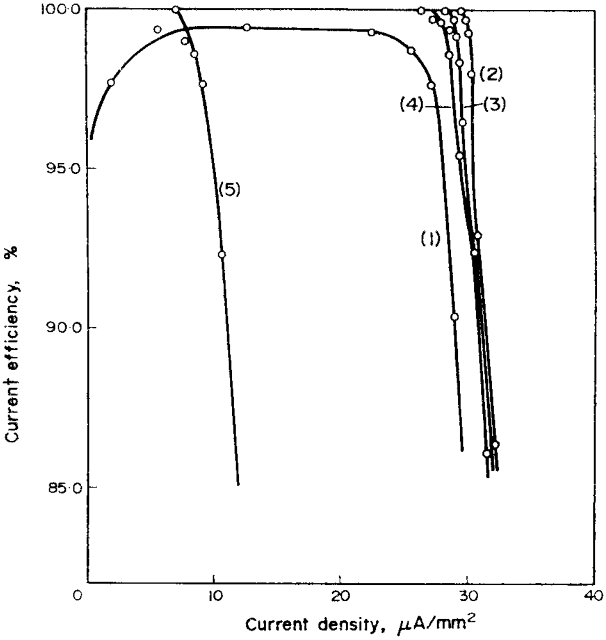

FIG. 2.—Current-efficiency curves for electrogeneration of octacyanomolybdate(V) as a function of current density and supporting electrolyte composition.
(1) In 0·75 or 1·25*M* potassium carbonate. (2), (3), (4) In potassium carbonate–bicarbonate buffer solutions, molar ratio: 0·2/1·5, 0·4/1·5, 1·3/1·3, respectively. (5) In potassium carbonate–bicarbonate buffer solution, molar ratio: 4·6/0·3.

even though in such alkaline conditions the redox potential of the Ce(IV)/Ce(III) system is lowered considerably. The apparent redox potential observed (uncorrected for liquid junction potential) in 3*M* potassium carbonate was −0·17 V (*vs.* S.C.E.) at 20°C.

Moderately satisfactory results were obtained when the carbonate concentration was lowered to 0·75–1·25*M*, but even in those conditions the precision of the results was notably affected by the decomposition expressed in reaction (1). The apparent redox potentials of the Ce(IV)/Ce(III) system in this range of potassium carbonate concentrations were −0·008 and −0·10 V (*vs.* S.C.E.) respectively, at 20°C.

Concentrations of carbonate less than 0·75*M* are not recommended if it is hoped to develop a method which permits the determination of successive samples of cerium in the same cell, because the resultant precipitation of cerium carbonates has an appreciable effect on the velocity of reaction (2).

The determination was also run in 2*M* bicarbonate solution, but was not satisfactory, owing to the insolubility of the cerium in this medium.

Better results were obtained when the determinations were run in concentrated buffer solutions of potassium carbonate–bicarbonate. Such solutions guarantee a quantitative current efficiency in the electrogeneration of the oxidant, the alkalinity is not excessive and thus largely avoids reaction (1), and there is an adequate concentration of the free carbonate necessary for complexing the cerium ions. The apparent redox potential of the Ce(IV)/Ce(III) system varied between the limits of +0·05 and

$-0{\cdot}11$ V (*vs.* S.C.E.), as the molar ratio of carbonate to bicarbonate was varied from 0·2/1·5 to 4·6/0·3.

The determinations that gave the most satisfactory results (error and standard deviation of $\pm 0{\cdot}3\%$) were those run in a carbonate–bicarbonate medium of 0·4/1·5 molar ratio. With lower molar ratios the errors were predominantly negative, which would seem related to the low concentration of available free carbonate. Higher ratios, from 1·3/1·3 to 4·6/0·3, gave results in which the error fluctuated between $\pm 1\%$ at the lower limit to $+83\%$ at the upper, indicating that such conditions are unsatisfactory.

Effect of the octacyanomolybdate(IV) concentration. In a carbonate–bicarbonate medium with a 0·4/1·5 molar ratio, and a current density of 17 μA/mm^2, the octacyanomolybdate(IV) concentration can be varied between $4{\cdot}0 \times 10^{-3}$ and $4{\cdot}4 \times 10^{-2}M$. Concentrations lower than $4{\cdot}0 \times 10^{-3}M$ give rise to high positive errors, since in such conditions the density of the limiting diffusion current of the octacyanomolybdate(IV) is less than the density of the applied current, thereby diminishing considerably the current efficiency in the electrogeneration of the oxidizing agent. According to the empirical formula of Lingane,[11] the minimum concentration of the octacyanomolybdate(IV) necessary to guarantee a quantitative current efficiency in these conditions is $3{\cdot}5 \times 10^{-3}M$, which is in good agreement with the value of $4{\cdot}0 \times 10^{-3}M$ obtained experimentally.

Concentrations greater than $4{\cdot}4 \times 10^{-3}M$ reduce considerably the precision of the determinations, because the slowness with which the equivalent potential is reached makes its estimation imprecise. For the rest of this study a $7{\cdot}5 \times 10^{-3}M$ concentration was used.

Effect of the Ce(IV) concentration. In order to determine the feasibility of applying this method to successive determinations of cerium in the same cell, the optimum conditions previously established were used in studying the effect of the concentration of Ce(IV) present in solution as the carbonate complex. We observed that in the range studied (7×10^{-6} to 6×10^{-4} mole), Ce(IV) does not interfere, so that 7 μmole of Ce(III) can be determined in the presence of 6×10^{-4} mole of Ce(IV), with an accuracy and precision of $\pm 0{\cdot}3\%$. This is equivalent to saying that in the same cell 80 analyses can be performed without the electrolyte having to be changed, provided that the quantity of cerium to be determined (7 μmole) is contained in a volume no larger than 0·1 ml (acidity of solution 0·05*N*). Under these conditions the dilution and the lowering of the concentration of free carbonate present in the solution, due to repeated addition of sample, are negligible.

Effect of the temperature. Since the stability of octacyanomolybdate(V) in aqueous solutions is temperature dependent,[17] this effect was also evaluated. Determinations were run at 0, 20, 30, 40 and 50°. In general there were no appreciable differences in the range 20–40°. The analyses run at 50° gave positive errors of 1 and 2%, which were attributed to decomposition of the oxidizing agent. There was a noticeable instability of the equivalent point potential when the electrolysis current was interrupted, which would result from this loss of oxidant.

The runs at 0° gave positive errors of the order of $+30\%$. This deviation could be related in part to a possible reduction of the velocity of reaction (2), but more fundamentally it would seem to be due to a lowered current efficiency. When a current density of 17 μA/mm^2 was applied in the electrogeneration of oxidizing agent, the

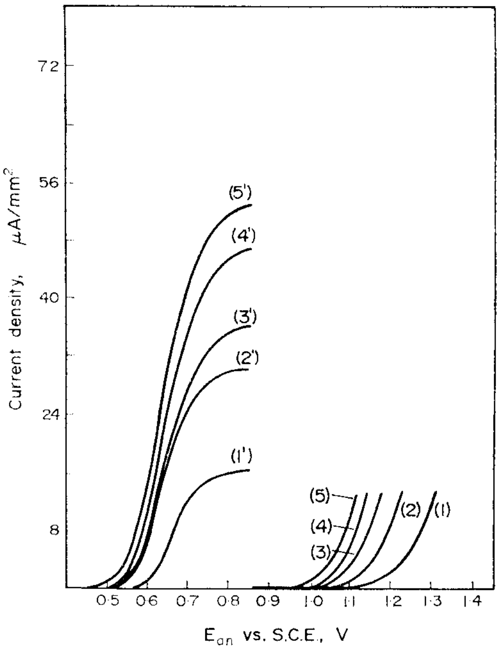

Fig. 3.—Current–anode potential curves for oxidation of octacyanomolybdate(IV) in potassium carbonate–bicarbonate buffer solution (molar ratio 0·4/1·5). Effect of temperature.
(1), (2), (3), (4), (5): Supporting electrolyte alone at 0, 20, 30, 40, 50°C, respectively.
(1′), (2′), (3′), (4′), (5′): Supporting electrolyte and octacyanomolybdate(IV) at 0, 20, 30, 40, 50°C, respectively.

current-potential and current efficiency curves shown in Figs. 3 and 4 respectively were obtained, and these show that the current efficiency in such conditions is reduced to 90%.

Interferences. Mn(II), V(IV) and U(IV) interfere seriously because they are oxidized along with Ce(III), while V(V), U(VI), Br^- and Cl^- do not interfere. It is reasonable to expect that such elements as Mn, Co, Ni, Fe, Cr, Cu, Cd, Zn, Al, Ca, and Mg would interfere, since they would be precipitated in the experimental conditions used and thus should be separated previously. Ion-exchange according to the method of Ahluwalia and Korkisch[18] is recommended for this separation.

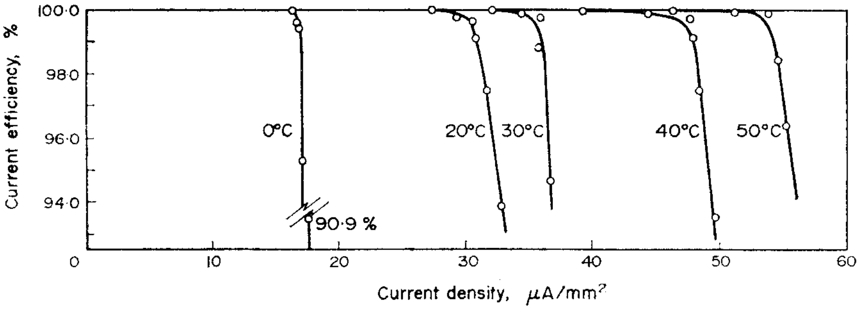

Fig. 4.—Current efficiency for electrogeneration of octacyanomolybdate(V) in potassium carbonate–bicarbonate buffer solution (molar ratio 0·4/1·5) as a function of current density and temperature.

TABLE I.—DETERMINATION OF Ce(III) WITH ELECTROGENERATED OCTACYANOMOLYBDATE(V).

Ce(III)	μmole	Difference	
Taken	Found	μmole	%
0·89	0·90	0·01	1·1
0·94	0·95	0·01	1·1
1·06	1·07	0·01	1·0
1·45	1·47	0·02	1·4
1·52	1·54	0·02	1·3
1·62	1·64	0·02	1·2
2·87	2·90	0·03	1·0
3·00	3·03	0·03	1·0
3·03	3·07	0·04	1·3
4·71	4·75	0·04	1·3
5·11	5·15	0·04	0·8
5·28	5·29	0·01	0·2
5·83	5·82	−0·01	−0·3
6·37	6·38	0·01	0·2
6·47	6·47	—	—
7·43	7·41	−0·02	−0·3
7·49	7·49	—	—
7·63	7·65	0·02	0·3

Effect of the Ce(III) concentration. Table I shows the results for various concentrations of cerium. Under optimum conditions—a solution of carbonate–bicarbonate of molar ratio 0·4/1·5, temperature 20–40°C, concentration of octacyanomolybdate(IV) $7\cdot5 \times 10^{-3}M$, Ce(IV) less than 6×10^{-4} mole—the method proposed permits the determination of 1–5 μmole with an accuracy of ±1·4%, and of 6–8 μmole with an accuracy of ±0·3%.

Precision. The relative standard deviation was ±0·3% for the concentration range studied, as determined by tabulation of 18 values of the ratio Ce taken/Ce found.

Applications

In conjunction with the ion-exchange technique proposed by Ahluwalia and Korkisch,[18] the method described here would permit successive determinations of cerium in steels, iron alloys, cast iron and monazite sands.

Zusammenfassung—Die coulometrische Bestimmung von Cer(III) mit Octacyanomolybdat(V) wurde in konzentrierten Carbonat-Bicarbonat-Pufferlösungen ausgeführt. Die Stromausbeute bei der elektrolytischen Erzeugung von Octacyanomolybdat und die besten Bedingungen für analytische Bestimmungen von Mikromengen Cer wurden untersucht.

Résumé—On a réalisé le dosage coulométrique de Ce(III) au moyen d'octacyanomolybdate(V) dans des solutions tampons concentrées carbonate–bicarbonate. On a étudié l'efficacité du courant pour l'électrogénération d'octacyanomolybdate(V) et les conditions optimales pour les déterminations analytiques de microquantités de cérium.

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FILM STRIPPING VOLTAMMETRY

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Summary—Film stripping voltammetry is a new electrochemical analytical method consisting in concentrating the test substance in the form of a metal or a sparingly soluble compound on the electrode surface and subsequently recording the current for electrodissolution of the deposit. The method has been worked out for determination of metal ions, anions and variable valence ions, with sensitivities as low as $10^{-9}M$. As indicator electrodes, solid, usually graphite, electrodes and stationary mercury electrodes are used.

NOTATION

F	is the faraday, C/meq.
n	the number of electrons
S	the electrode area, cm^2
D	the diffusion coefficient, cm^2/sec
δ_1	the diffusion layer thickness, cm
μ	the kinetic layer thickness, cm
C_1^0	the ion concentration in the solution, $mole/cm^3$
$C^{\circ}_{1\min}$	the minimum bulk concentration of the metal ions from which the compound deposited may be formed on the electrode surface, mole/ml
τ_1	the concentration time, sec
Q	the amount of the metal (compound) deposited, expressed in Q-units, C
i	the current, in A
I_M	the current maximum
k_s	the rate constant of the electrode process at the standard potential, cm/sec
α, β	the coefficients of the electrode transfer process
γ	the proportionality coefficient, C^{-1}
a, a_∞	the activities of the deposit on the electrode and of the macrophase, respectively, mole/ml
$a_\infty{}^1$	$= 1$
ϕ	is the electrode potential, V
ϕ_1	is the original value of the potential, V
ϕ^0	is the standard potential, V
V	the rate of potential change, V/sec
t	the time, sec
L	the solubility product for the compound formed on the electrode
k_1, k_2	the constants of the forward and reverse chemical reactions, respectively, sec^{-1}

$k_2/k_1 = \sigma$
$\sigma f = \sigma'$
$f =$ activity coefficient
$l =$ the film thickness, cm

THE PROCESSES of electrolytic deposition and dissolution of metals and chemical compounds have been made the basis of a new electrochemical method of analysis in which trace amounts of the material being determined are first concentrated on an electrode as a solid film, and subsequently removed by controlled dissolution.

This technique is called film stripping voltammetry (film polarography) since the main source of information is the dissolution curve (polarogram) or other record of some variable during the process of electrolytic dissolution of the film

At present there exist three variants of film polarography, which correspond to the following types of electrode reactions:

(1) discharge-ionization of metals on an inert electrode (film stripping voltammetry for metals, FSVM),

(2) electro-oxidation or reduction of variable valence ions accompanied by the formation of a sparingly soluble compound on the surface of an inert electrode with subsequent electrodissolution of these compounds (film stripping voltammetry for variable valence ions, FSVI),

(3) anodic polarization of the electrically active electrode, resulting in the formation of sparingly soluble compounds on its surface followed by electroreduction of the compound (film stripping voltammetry for anions, FSVA).

The first is usually called anodic stripping voltammetry (ASV), and the last cathodic stripping voltammetry (CSV).[1]

The development of the new variant of the method, variant (2), has revealed its limitations, as both cathodic and anodic reactions may result in concentrating the variable valence ions, and the process may be either anodic or cathodic. Because of this, it is preferable to use the nomenclature outlined, rather than refer to the electrode reaction in terms of direction of the current causing polarization.

Unfortunately, the literature on film stripping voltammetry has not been collated. Only a few references concerning the determination of the noble metals (by ASV) and certain anions (by CSV) have been included in reviews published.[1]

The increasing number of papers dealing with film stripping voltammetry suggests that there is a need for a review of the principles of the method, its analytical possibilities and its practical applications.

This paper reviews the recent literature and the results of unpublished work by the author and collaborators.

FILM STRIPPING VOLTAMMETRY FOR METALS

In this variation of the method the concentration step involves reduction of the metal ion under stationary hydrodynamic conditions at a potential corresponding to the diffusion-controlled limiting current. The amount of metal thus deposited on the electrode surface is expressed by the following simple relationship:

$$Q = nFSD\frac{C_1{}^0\tau_1}{\delta_1}. \tag{1}$$

This dependence of the amount of metal deposited, on the ion concentration and the electrolysis time, has been experimentally corroborated with electroreduction of ions of lead, cadmium, gold, antimony, tin, *etc.*

The metal ion concentration is determined by measuring the maximum electrodissolution current for the deposit when the stripping potential is linearly varied.[2]

Several papers have described the electrodissolution of a metal from the surface of an inert electrode. Thus, Nicholson,[3] who first proposed the technique of FSVM, has considered the process of anodic dissolution of a metal film from the surface of a foreign solid electrode, assuming that the deposit forms an incomplete monolayer on a statistically homogeneous surface and that the activity of the layer is determined by the part of the surface occupied. The calculation is valid only for a reversible process. Proceeding from the same assumptions the author has considered a process of electrodissolution of thin metal layers from the surface of an inert electrode for the case where the electrode process is irreversible.[4]

The problem of stripping the metal from the surface of an inert electrode in the general case, independent of either the metal layer thickness or the kinetics of the process, has been solved in a later series of papers.[5–9]

Distribution of the metal ion concentration (C) in the layer adjacent to the electrode is expressed by the differential equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{2}$$

with the boundary and initial conditions having the form

$$-\frac{D}{k_s}\cdot\left(\frac{\partial C}{\partial x}\right)_{x=0} = a_\tau \exp\left[\frac{\beta nF}{RT}(\varphi_1 - \varphi^0 + Vt)\right] - c(0, t)\exp\left[-\frac{\alpha nF}{RT}(\varphi_1 - \varphi^0 + Vt)\right] \tag{3}$$

$$a_\tau = a_\infty\left\{1 - \exp\left[-\gamma\left(Q_0 - \int_0^t i\,d\tau\right)\right]\right\}; \quad c(x, 0) = c^0; \quad c_{x\to\infty} = c^0 \tag{4}$$

where

$$i = -nFSD\left(\frac{\partial c}{\partial x}\right)_{x=0}; \qquad \phi = \phi_1 + Vt.$$

The equations have been solved by computer for various combinations of parameters and information has been obtained concerning the following factors connected with the electrode process: Current dependence of the potential of the electrode, the maximum current value and the potential of the maximum on the polarization curve, ion concentration distribution as a function of time, and the validity of inequalities characteristic of electrodissolution kinetics.*

For an irreversible electrode process the polarization curve equation is obtained in the analytical form from equation (3).

The principal relationships between the parameters for the electrodissolution of metals are shown in Tables I and II. As an example Fig. 1 shows the calculated stripping-voltammograms corresponding to various values of parameters. From this figure and the equations given in the tables some common regularities follow which are inherent in voltammograms describing the process of metal electrodissolution. The maximum of the current is strongly pronounced. For thin films its

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* The process is regarded as irreversible when the rate at which metal ions are discharged may be neglected compared with the ionization rate of metal atoms. This is valid (*a*) when anodic electrode polarization is sufficient or (*b*) when rate of removal of ionization product from the electrode surface is rapid compared with the ionization rate.

TABLE I.—PRINCIPAL RELATIONSHIPS BETWEEN THE PARAMETERS OF THE REVERSIBLE PROCESS OF STRIPPING A METAL FROM AN INERT ELECTRODE SURFACE

Thin films: rotating electrode*

$$i = \frac{Q_0}{\tau_1} \exp\left[\frac{nF}{RT} Vt - \frac{RT}{nFV\tau_1}\left(\exp \frac{nF}{RT} Vt - 1\right)\right]$$

$$I_m = \frac{nF}{RT} VQ_0 \exp\left(\frac{RT}{nFV\tau_1} - 1\right)$$

$$Vt_m = \frac{RT}{nF} \ln \frac{nF}{RT} \tau_1 + \frac{RT}{nF} \ln V$$

Stationary electrode

Thin films

$$I_m = 0{\cdot}79 \frac{nF}{RT} V_0 Q \exp\left(\frac{\delta_1}{\sqrt{\frac{nF}{RT} D V \tau_1}} - 1\right)$$

$$Vt_m = \frac{RT}{nF} \ln \frac{\tau_1 \sqrt{\frac{nF}{RT} D}}{\delta_1} + \frac{RT}{2nF} \ln V$$

Thick films

$$I_m = -0{\cdot}93 \frac{nF}{RT} VQ_0' + 0{\cdot}93 \frac{nF}{RT} VQ_0$$

* The equations are obtained on the assumption that at any given moment the electrode potential is at equilibrium in relation to the concentration of ions determining the potential near the electrode and to the activity of the metal on its surface.[8]

Because $RT/nFV\tau_1$ and $\delta_1/\tau_1\sqrt{nFDV/RT}$ are $\ll 1$, the values of the relative exponent sapproximate to $e^{-1} \sim 0{\cdot}37$.

TABLE II.—PRINCIPAL RELATIONSHIPS BETWEEN THE PARAMETERS OF THE IRREVERSIBLE PROCESS OF STRIPPING A METAL FROM AN INERT ELECTRODE SURFACE

Thin films

$$I_m = \frac{nF}{RT} \beta VQ_0 \exp\left[\frac{k_s s a_\infty \gamma RT}{\beta V}\left(\frac{\delta_1 f}{a_\infty' \gamma nFSD\tau_1}\right)^\beta - 1\right]$$

$$Vt_m = \frac{RT}{\beta nF} \ln \frac{\beta}{k_s a_\infty}\left(\frac{D\tau_1}{\delta_1 f}\right)^\beta (\gamma S)^{\beta-1} \frac{(nFa_\infty')^\beta}{RT} + \frac{RT}{\beta nF} \ln V$$

Thick films

$$I_m = -0{\cdot}93 \frac{nF}{RT} \beta VQ_0' + 0{\cdot}835 \frac{nF}{RT} \beta VQ_0$$

Because $\frac{k_s s a_\infty \gamma RT}{\beta V}\left(\frac{\delta_1 f}{a_\infty' \gamma nFSD\tau_1}\right)^\beta \ll 1$, the value of the corresponding exponent approximates to $e^{-1} \sim 0{\cdot}37$.

value is directly proportional to the amount of metal on the electrode and to the metal ion concentration in solution in the case of electrodissolution of thin films. In the case of electrodissolution of both thick[10] and thin films the chief characteristic is the linear relationship of the current maximum to the amount of metal on the electrode and to the metal ion concentration in solution. This opens up the possibility

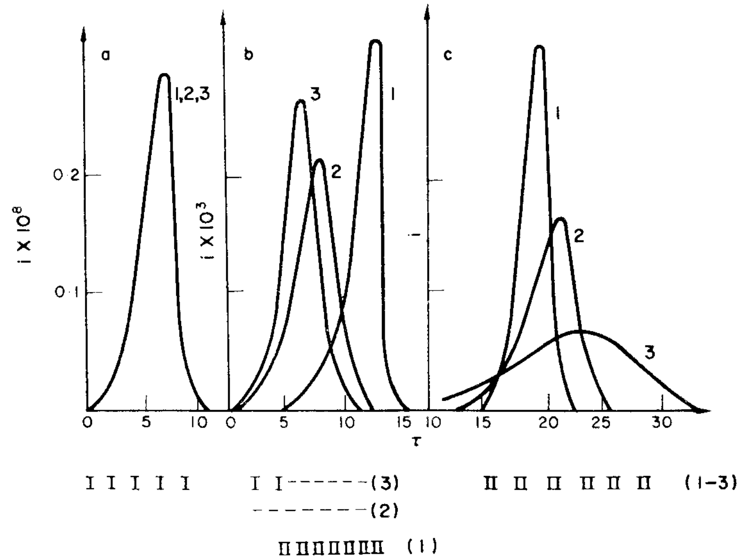

FIG. 1.—Stripping voltammograms, calculated.
$k_s = 1$ (*a*), 1×10^{-5} (*b*), 1×10^{-8} cm/sec (*c*); $\beta = 0{\cdot}9$ (*1*); $0{\cdot}5$ (*2*); $0{\cdot}2$ (*3*); $C_1^0 = 0{\cdot}25 \times 10^{-8}$ mole/ml; $V = 0{\cdot}1$ V/sec. The limiting stages for the process are indicated by I—metal ion removal from the electrode surface, II—metal atom ionization, (—)—the rates of the forward and reverse reactions are commensurable.

of using the electrodeposition of metal with subsequent recording of the electrodissolution current, as an analytical method.

Information concerning the kinetics may be obtained from the position of the curve in relation to the potential axis, the relationship between the potential of the curve maximum and the potential sweep rate, the slope of the linear parts of the curves in coordinates I_M–Q_0 and the difference in potentials of ascending and descending portions of the curve.

Figure 2 shows experimental voltammograms for the electrodissolution of silver from graphite and platinum electrodes. The dependence of the maximum current on the amount of metal on the electrode and on the ion concentration in solution corresponds to the theoretically predicted,[8] and the proportionality between the two quantities makes the method useful as an analytical tool. Analytical applications of the technique have been discussed in a recent review by Barendrecht.[1] The voltammograms for electrodissolution of some metals are presented in Fig. 3; Table III summarizes certain characteristics of ionization of metals on a graphite electrode.[2] Table IV contains new data on practical analytical applications of FSVM.

FILM STRIPPING VOLTAMMETRY FOR VARIABLE VALENCE IONS

In the presence of substances capable of forming a sparingly soluble compound with the product of electro-oxidation or electroreduction, ions of variable oxidation state may be concentrated on an electrode. The process may be described by the equations:[23,24]

$$M^{m+} \rightleftharpoons M^{(m\pm n)+} \pm ne$$

$$M^{(m\pm n)} + (m \pm n)A^- \rightleftharpoons MA_{m\pm n} \downarrow$$

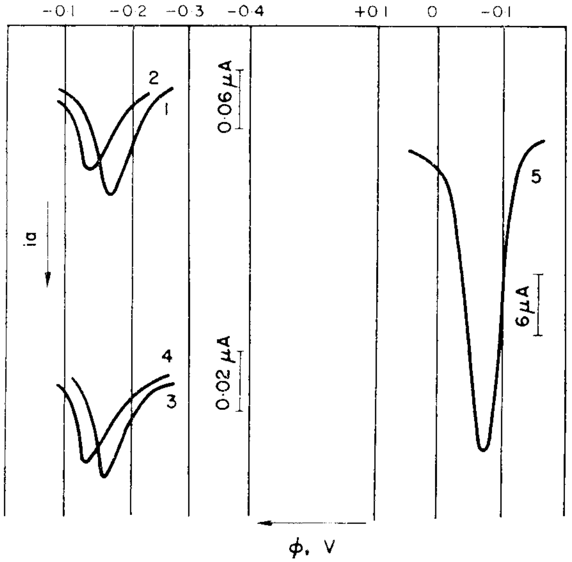

FIG. 2.—Stripping voltammogram of silver as recorded on the rotating (1–3) and stationary (2, 4, 5) graphite (1, 2, 5) and platinum (3, 4) electrodes.

The solutions contain 0·1M KNO_3 + 5 × $10^{-7}M$ $AgNO_3$ (1–4) and 1M KNO_3 + 5 × $10^{-5}M$ $AgNO_3$ (5); φ_{el} = −0·6 V (*vs* saturated mercury sulphate electrode K_2SO_4), τ_1 = 1 min. V = 0·01 V/sec.

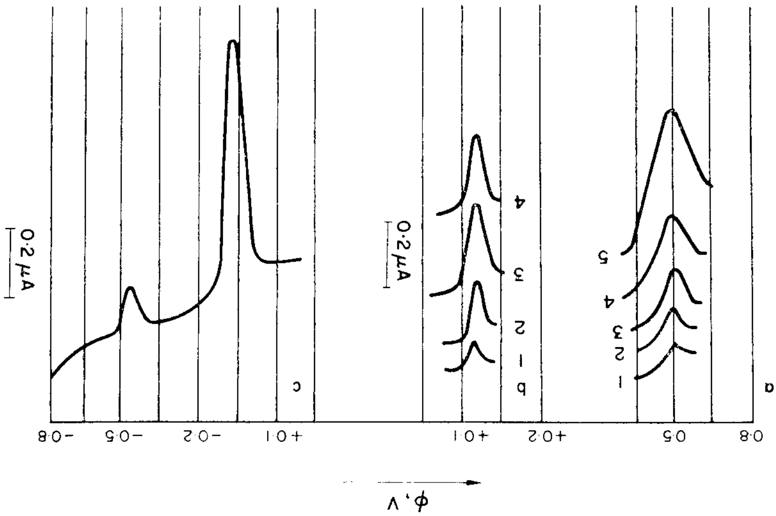

FIG. 3.—Stripping voltammograms of the metals deposited on the graphite electrode from the solutions given below.

(*a*) 1M HCl + xM $HAuCl_4$; $x = 2 \times 10^{-8}$ (*1*); 3×10^{-8} (*2*); 5×10^{-8} (*3*); τ_1 = 15 min; $x = 5 \times 10^{-7}$ (*4*); 1×10^{-6} (*5*); τ_1 = 1 min; φ_{el} = −0·2 V.

(*b*) 0·1M KCl + 0·1M HCl + xM $BiCl_3$; $x = 1 \times 10^{-8}$ (*1*); 3×10^{-8} (*2*); τ_1 = 10 min; $x = 5 \times 10^{-7}$ (*3*); 1×10^{-6} (*4*); τ_1 = 1 min; φ_{el} = −0·4 V. (*c*) 0·1M KCl + 0·1M HCl + 5 × $10^{-7}M$ $Pb(CH_3COO)_2$ + 1·5 × $10^{-6}M$ $BiCl_3$; τ_1 = 1 min; φ_{el} = −0·8 V.

TABLE III.—SOME CHARACTERISTICS OF PROCESSES $M^{n+} + ne \rightleftarrows M$ ON THE GRAPHITE ELECTRODE[2]

Metal ion	Indifferent electrolyte	$\varphi_{1/2}$, V	φ_{el}, V	φ_m, V
Au(III)	1M HCl	+0·5	−0·2	+0·5
	1M HNO_3	+0·75	−0·2	+0·85
Ag(I)	1M KNO_3	+0·05	−0·2	+0·10
Cu(II)	1M KNO_3	−0·35	−0·6	−0·05
	0·02M $CO_2H(CHOH)_2CO_2H$ + 0·02M NH_4Cl + NaOH, pH 9		−0·8	−0·4
	1M KOH + 0·1M $CO_2H(CHOH)_2CO_2H$		−1·6	−0·5
	1M KOH + 1M NaSCN		−1·3	−0·45
Bi(III)	0·1M NH_4Cl	−0·2	−0·5	−0·15
	0·1M KCl + 0·1M HCl	−0·20	−0·4	−0·05
	0·1M NH_4Cl	−0·2	−0·4	−0·1
Pb(II)	0·1M HCl	−0·6	−1·0	−0·55
	0·1M NH_4Cl	−0·6	−0·8	−0·55
	20% $C_3H_4(OH)(CO_2H_3)$	−0·7	−1·0	−0·45
Sb(III)	1M $CH_3CO_2NH_4$	−0·3	−1·0	−0·25
	1M HCl	−0·25	−0·5	−0·05
Sn(IV)	1M NH_4Cl	−0·75	−1·2	−0·50
	1M HCl	−0·6	−1·2	−0·50
	20% $C_3H_4(OH)(CO_2H_3)$		−1·2	−0·25
Cd(II)	0·1M HCl	−0·8	−1·2	−0·75
	1M KCl		−1·2	−0·75
Hg(II)	1M KSCN	−0·25	−0·6	−0·1
	0·1M KNO_3	−0·1	−0·4	+0·1
In(III)	1M NH_4SCN	−0·9	−1·4	−0·7
	0·1M KCl	−0·9	−1·3	−0·65
Il(I)	0·2M $(NH_4)_2SO_4$ + NH_4OH, pH 8	−0·95	−1·4	−0·8
	0·1M NaSCN		−1·2	−0·4
Ni(II)	0·1M NH_4OH + 0·1M NH_4Cl	−1·1	−1·2	−0·5
	1M KNO_3 + 0·001M HNO_3		−1·2	−0·1
	0·1M NaSCN		−1·2	−0·45
	0·2M NH_4OH		−1·2	−0·4
Co(II)	0·1M K_2SO_4		−1·4	−0·1
	0·1M $CO_2H(CHOH)_2CO_2H$ + 1M KOH		−1·6	−0·6
	1M KOH + 0·1M NaSCN		−1·2	−0·7
Fe(III)	1M KOH + 0·01M $CO_2H(CHOH)_2CO_2H$		−1·4	−0·85
	0·05M $C_7H_5O_6S$ Na, pH 5		−1·6	−0·55
Zn(II)	0·1M KOH		−1·6	−1·35
Mn(II)	0·2M $CO_2H(CHOH)_2CO_2H$ + 1M KOH + 0·1M $N_2H_4H_2SO_4$		−2·0	+0·1

Note: $\varphi_{1/2}$ values *vs*. SCE for metal concentration of 1×10^{-5}–$1 \times 10^{-4}M$ and φ_m for 1×10^{-7}–$1 \times 10^{-6}M$ are approximate, the rate of potential change being 0·017 V/sec.

where M^{m+} and $M^{(m\pm n)+}$ are the oxidation states of element M, and A^- is the substance forming a sparingly soluble compound with M ions. For $(m + n)$e the process is anodic; for $(m - n)$e the process is cathodic.

A necessary condition for concentrating the $M^{(m\pm n)+}$ ions on the electrode-solution interface is that the rate of chemical reaction should be high enough in comparison with the rate of release of $M^{(m\pm n)+}$ ions into solution. Also, A^- should be selective towards that oxidation state of the ions that is formed during the electrode reaction,

TABLE IV.—ANALYTICAL APPLICATIONS OF FILM STRIPPING VOLTAMMETRY FOR METALS

Test compound	Test element	Stripping method	Electrode type	Indifferent electrolyte	Sensitivity		Ref.
					M	%, W/w	
Salts of alkali and alkaline earth metals	Ag	LS	Graphite (ED-6)*	Test salt solution		1×10^{-5}	11
$Pb(NO_3)_2$, $Pb(CH_3COO)_2$	Ag	LS	Graphite (ED-6)*	Test salt solution		1×10^{-5}	12
Thiocarbamide†	Ag	LS	Graphite (ED-6)*	$0{\cdot}5M\ CH_3COONa + HNO_3$, pH 4		5×10^{-6}	12
KNO_3	Ag	LS	Graphite, paste	$0{\cdot}2M\ KNO_3$	$2{\cdot}5 \times 10^{-9}$		13
KNO_3	Ni	LS	Pt, Au	$0{\cdot}1M\ KNO_3 + 0{\cdot}01M\ KSCN$	5×10^{-8}		14
KNO_3	Ag	LS	Graphite (paraffin)	Test salt solution	4×10^{-9}		15
	Ag	DLS	Graphite (paraffin)	Test salt solution	$1{\cdot}5 \times 10^{-10}$		16
HNO_3	Cu, Pb	OP	Graphite (ED-6)	$0{\cdot}1M\ HNO_3 + 1 \times 10^{-5}M\ Hg(NO_3)_2$	1×10^{-8}	$1{\cdot}5 \times 10^{-6}$	17
KNO_3	Tl	DLS	Graphite (paraffin)	Test salt solution	$5{\cdot}5 \times 10^{-8}$		16
	Pb				$4{\cdot}5 \times 10^{-8}$		16
KCl	Cd	DLS	Graphite (paraffin)	$0{\cdot}0002M$ KCl	6×10^{-11}		18
$C_2O_4(NH_4)_2.H_2O$ and $C_2O_4K_2$	Hg, Ag	LS	Graphite (ED-6)	$1M$ KSCN			
	Cu + Bi			$1{\cdot}5\%\ K_3Cit$ + test salt		$(2–4) \times 10^{-6}$	19
	Pb, Cd			$1{\cdot}2 \times 10^{-4}M\ Hg(NO_3)_2$ + test salt		5×10^{-8}	
HCl	Pb, Cd, Cu + Bi	LS	Graphite (ED-6)	$0{\cdot}5M\ HCl + 1 \times 10^{-4}M\ Hg(NO_3)_2$		1×10^{-7}	
$Er_2(MoO_4)_3$,† $Y_2(MoO_4)_3$, $Nd_2(MoO_4)_3$	Fe	LS	Graphite (ED-6)			10^{-4}	20
KSCN	Hg	LS	Graphite (wax)	$0{\cdot}1M$ KSCN	4×10^{-9}		21
CdS, ZnS	Cu	LS	Graphite (ED-6)	$CdCl_2$, $ZnCl_2$	1×10^{-7}	3×10^{-6}	
$(NH_4)_2MoO_4$†	Co	LS	Graphite (ED-6)	$1{\cdot}25M\ NaSCN + 2{\cdot}5M\ KOH$	2×10^{-7}	1×10^{-5}	
$(NH_4)_2MoO_4$†	Fe	LS	Graphite (ED-6)	$1{\cdot}5M\ KOH + 0{\cdot}006M\ H_2Tart + 0{\cdot}001M\ Na_2S$	2×10^{-7}	1×10^{-5}	

Table IV (*Cont.*)

Test compound	Test element	Stripping method	Electrode type	Indifferent electrolyte	Sensitivity		Ref.
					M	%, W/w	
$(NH_4)_2MoO_4$†	Cu	LS	Graphite (ED-6)	$1M$ KOH + $0{\cdot}04M$ H_2Tart + $0{\cdot}12M$ NH_4Cl	2×10^{-7}	1×10^{-5}	
H_3Cit§ and H_2Tart‡	Sn Sb	LS	Graphite (ED-6)	$1M$ H_3Cit (H_2Tart) + $8M$ HCl + $1 \times 10^{-4}M$ $Hg(NO_3)_2$	2×10^{-7}	1×10^{-5}	
	Pb	LS	Graphite (ED-6)	$1M$ H_3Cit(H_2Tart) + $1 \times 10^{-4}M$ $Hg(NO_3)_2$	1×10^{-7}	1×10^{-5}	
	Fe	LS	Graphite (ED-6)	$1M$ K_3Cit(K_2Tart) + KOH + $5 \times 10^{-3}M$ Na_2S, pH 10	2×10^{-7}	1×10^{-5}	
HCl	Au	LS	Carbon paste	$0{\cdot}1M$ HCl		10^{-10}	22
HNO_3	Cu	OP	MFE(Ag)	$0{\cdot}1M$ HNO_3			1
Li_2SO_4	Hg	OP	Carbon paste	$1{\cdot}8M$ Li_2SO_4 + $0{\cdot}1M$ KSCN			1
			Graphite (wax)	$0{\cdot}1M$ KSCN			21
Melted fluorides	Ni	OP	Pt	Melted fluoride			1
Cd	Sb	LS	Graphite (ED-6)	$CdCl_2$ + $2M$ HCl + $1 \times 10^{-4}M$ $Hg(NO_3)_2$	2×10^{-7}	5×10^{-5}	
Pb	Sb	OP	Graphite (ED-6)	$6M$ HCl + $0{\cdot}06M$ $Pb(NO_3)_2$ + $1 \times 10^{-4}M$ $Hg(NO_3)_2$	3×10^{-8}	5×10^{-5}	
Cd, Pb	Ag	LS	Graphite (ED-6)	$Me(NO_3)_2$ + HNO_3, pH 1	2×10^{-7}	2×10^{-5}	
Sn	Ag	LS	Graphite (ED-6)	$Sn(SO_4)_2$ + $5M$ H_2SO_4	5×10^{-7}	1×10^{-4}	

* ED-6—epoxy resin.

† The substance is heated and dissolved in the indifferent electrolyte.

‡ H_2Tart—tartaric acid.

LS—linear scan.

DLS—derivative stripping voltammetry with linear scan.

DLS—derivative stripping voltammetry with linear scan.

OP—oscillographic polarography.

§ H_3Cit—citric acid.

and indifferent towards the element in its original oxidation state (under the experimental conditions).

The sensitivity of the method is limited by the solubility of the compound formed on the electrode, and of course by the sensitivity of the current-measuring equipment.[25] The minimum concentration C_1^0 of M^{m+} at which a deposit is formed on the electrode is given by the relationship

$$C_1^0 \geqslant \frac{L}{C_{A^-}^{m\pm n}} \cdot \frac{\delta_1}{\mu} \cdot \tag{5}$$

The amount of the compound formed on the electrode under stationary hydrodynamic conditions with an applied potential sufficient to give the diffusion-limited current depends upon the M^{m+} concentration and the deposition time, and is given by

$$Q = nFSD \frac{C_1^0 - C_{1_{\min}}^0}{\delta_1} \tau_1 \tag{6}$$

or, when

$$C_1^0 \gg C_{1_{\min}}^0,$$

$$Q = nFSD \frac{C_1^0 \tau_1}{\delta_1} \,. \tag{7}$$

These equations are valid for the case where the film does not create a greater resistance than is due to diffusion.

The mechanism of electrodissolution of a compound from an enert electrode will depend on the electrical properties of the film. Compounds having rather high conductivity do not require the delivery of an electrically active substance to the electrode surface. The kinetics for such processes are determined by a relationship between the rate of electron transfer and the rate of product dispersion into the solution. Since this case is mathematically analogous to that already described where a metal is dissolved from the inert electrode, it will be given no special attention here.

For a film with low conductivity, the dissolution proceeds after a preliminary ionization stage which is accompanied by the arrival of electrochemically active ions at the electrode surface.

The irreversible process of film dissolution with a preceding chemical step has also been examined.[24] The process is described by the equations

$$D \frac{\partial^2 C_1}{\partial x^2} + k_1 C_2 - k_2 C_1 = 0 \tag{8}$$

$$\frac{\partial C_2}{\partial t} = k_2 C_1 - k_1 C_2 \tag{9}$$

with the boundary and initial conditions

$$C_2(x, 0) = C_2^0;\ C_1(x, 0) = \frac{C_2^0}{\sigma}$$

$$\left(\frac{\partial C_1}{\partial x}\right)_{x=0} = C_1(0, t)\, k e^{\beta v t}\,;\ \left(\frac{\partial C_1}{\partial x}\right)_{x=l} = 0. \tag{10}$$

Here C_1 and C_2 are the concentrations of $M^{(m\pm n)+}$ and $MA_{(m\pm n)}$ respectively, and

$$B = -\frac{\alpha nF}{RT}; \qquad k = \frac{k_s}{D_1}\exp\left[-\frac{\alpha nF}{RT}(\phi_1 - \phi_0)\right]$$

for the cathodic process and

$$B = \frac{\beta nF}{RT}; \qquad k = \frac{k_s}{D_2}\exp\left[\frac{\beta nF}{RT}(\phi_1 - \phi_0)\right]$$

for the anodic process.

In the calculation the concentration of anion A^- is included in the effective constant of the chemical reaction rate ($k_2 = k_2'[A^-]^{(m\pm n)}$).

Since in this case the chemical reaction is rapid compared to the diffusion process, the derivative of a concentration with respect to time is omitted from equation (8), ($k_1t, k_2t \gg 1$). Equation (9) does not contain a term describing diffusion of the solid substance $MA_{(m\pm n)}$ because this may be neglected. The boundary conditions express the fact that $M^{(m\pm n)}$ ions taking part in the electrode process are not supplied by the solution, and that their concentration gradient at the electrode surface is proportional to the electrodissolution current.

The maximum electrodissolution current is given by:

$$I_m = \frac{nFDS\gamma Q_0 a_\infty \sqrt{V}}{\sigma'\mu\sqrt{\pi k_1 \phi_m}\left(1 + \dfrac{1}{2B\phi_m}\right)} \tag{11}$$

$$I_m = \frac{(nFDS)^2 a_\infty \sqrt{V}}{\delta_1 \sigma' \mu \sqrt{\pi k_1 \phi_m}}(C_1^0 - C^0_{1_{min}})\tau_1 \tag{12}$$

$$I_m = \frac{(nFDS)^2 a_\infty \sqrt{V}}{\sigma'\mu\delta_1\sqrt{\pi k_1 \phi_m}} C_1 \tau_1^0. \tag{13}$$

It may be concluded from what has been said that the maximum current for electrodissolution of a compound is directly proportional to the amount of the compound and to the concentration of the electroactive ion, provided the latter is high compared with the minimum concentration which permits formation of a deposit. The more commensurable these values are, the closer the relationship between the maximum current and electroactive ion concentration approaches linearity. Under these conditions the method may be used analytically for the concentration of variable valence ions in the form of a solid film on an electrode.

The possibility of forming various compounds by cathodic or anodic reactions makes it possible to analyse multi-component systems without separation of the test element. It also permits concentration and determination of a series of elements in those cases where analysis is difficult or impossible by other methods.

In the FSVI method hydroxide ions,[23,26–32] and other inorganic ions[25] have been used as precipitants as well as various organic compounds.[33–38] The latter often act selectively, and as the compounds formed have rather low solubility, a high sensitivity may be achieved.

The reactions referred are summarized in Tables V and VI. The shapes of the voltammograms generally agree with those predicted.

TABLE V.—CONCENTRATION OF VARIABLE VALENCE IONS IN THE FORM OF COMPOUNDS WITH INORGANIC REAGENTS

Electroactive element	Electrode reaction	Solution	$\varphi_{1/2}$, V	φ_{el}, V	φ_m, V	$C_{1\,min}$, M	Ref.
Chromium	$CrO_4^{2-} + 4H_2O + 3e \rightleftharpoons Cr(OH)_3 + 5OH^-$	0·1M $NaOH + CrO_4^{2-}$	−0·8	−1·0	+0·17		
		0·05M $Na_2B_4O_7 + CrO_4^{2-}$, pH 9·2	−0·7	−1·0	+0·6	2×10^{-7}	
		$C_6H_8O_7 + NaOH + CrO_4^{2-}$, pH 5·2	−0·35	−0·5	+0·7	1×10^{-6}	30
		$KH_2PO_4 + NaOH + CrO_4^{2}$, pH 8·0	−0·35	−0·7	+0·7	1×10^{-7}	40
		0·4M NH_4Cl + 0·1M $NH_4OH + CrO_4^{2-}$	−0·45	−0·7	+0·6	4×10^{-8}	
		0·1M CH_3COOH + 0·1M $CH_3COONa + CrO_4^{2-}$	−0·1	−0·5	+0·9	2×10^{-6}	
		0·01M $H_2SO_4 + CrO_4^{2-}$	+0·15	−0·3	+1·15	1×10^{-5}	
	$Cr^{3+} + 8OH^- + M^{2+} \rightleftharpoons MCrO_4 + 4H_2O + 3e$	$Ba(OH)_2 + Cr^{3+}$	+0·2	+0·3	−0·6	6×10^{-6}	25
		$Pb(CH_3COO)_2 + Cr^{3+}$ + 0·1M CH_3COONa	+0·8	+1·0	−0·05	1×10^{-4}	
Cerium	$Ce^{3+} + 4H_2O \rightleftharpoons Ce(OH)_4 + 4H^+ + e$	0·1M CH_3COOH + 0·1M $CH_3COONa + Ce^{3+}$	+0·7	+1·0	+0·3	1×10^{-6}	29
Thallium	$Tl^+ + 3OH^- \rightleftharpoons Tl(OH)_3 + 2e$	0·35M $(NH_4)_2SO_4 + H_2SO_4 + Tl^+$	+1·15	+1·4	+0·35	2×10^{-6}	31
		0·35M $(NH_4)_2SO_4 + NH_4OH + Tl^+$, pH 7	+1·0	+1·2	+0·3	5×10^{-7}	

TABLE V (*Cont.*)

Electroactive element	Electrode reaction	Solution	$\varphi_{1/2}$, V	φ_{el}, V	φ_m, V	C_{1min}, M	Ref.
		$0{\cdot}35M\ (NH_4)_2SO_4 + NH_4OH + Tl^+$, pH 8	+0·8	+1·1	+0·2	2×10^{-6}	
		$0{\cdot}35M\ (NH_4)_2SO_4 + NH_4OH + Tl^+$, pH 9	+0·7	+0·9	+0·15	3×10^{-6}	
		$0{\cdot}35M\ (NH_4)_2SO_4 + NH_4OH + Tl^+$, pH 10	+0·55	+0·8	+0·1	9×10^{-5}	
Manganese	$Mn^{2+} + 4OH^- \rightleftharpoons Mn(OH)_4 + 2e$	$0{\cdot}1M\ HNO_3 + Mn^{2+}$	1·2	1·3	0·9	5×10^{-7}	27, 41
		$2M\ (NH_4)_2SO_4 + H_2SO_4 + Mn^{2+}$, pH 3	0·9	1·1	0·7		
		$2M\ (NH_4)_2SO_4 + H_2SO_4 + Mn^{2+}$, pH 4	0·8	1·0	+0·65		
		$2M\ (NH_4)_2SO_4 + H_2SO_4 + Mn^{2+}$, pH 5	0·75	0·9	0·25		
		$2M\ (NH_4)_2SO_4 + NH_4OH + Mn^{2+}$, pH 7	0·5	0·7	0·15		
		$2M\ (NH_4)_2SO_4 + NH_4OH + Mn^{2+}$, pH 8	0·25	0·5	0·10		
		$2M\ (NH_4)_2SO_4 + NH_4OH + Mn^{2+}$, pH 9	0·15	0·4	0·05		
Iron	$Fe^{2+} + 3OH^- \rightleftharpoons Fe(OH)_3 + e$	$H_3BO_3 + NaOH$, pH 8		−0·05	−0·05	1×10^{-7}	32

TABLE VI.—CONCENTRATION OF THE VARIABLE VALENCE IONS IN THE FORM OF COMPOUNDS WITH ORGANIC REAGENTS

Element	Electrode reaction	Solution	$\varphi_{1/2}$, V	φ_{el}, V	φ_m, V	$C^{\circ}_{1\,min}$, M	Ref.
Tin	$Sn^{4+} + 2(C_2H_5O)_2PS_2{}^{2-} + 2e \rightleftharpoons Sn[(C_2H_5O)_2PS_2]_2$	$1{\cdot}0M$ HCl $+ 1{\cdot}5 \times 10^{-3}M$ $[(C_2H_5O)_2PS_2]Ni + Sn^{4+}$	$-0{\cdot}2$	$-0{\cdot}4$	$-0{\cdot}05$	5×10^{-8}	34
Cobalt	$Co^{2+} + 3RH \rightleftharpoons CoR_3 + 3H^+ + e$; RH = nitrosonaphthol	$0{\cdot}4M$ $NH_4OH + 0{\cdot}05M$ NH_4Cl $+ 1{\cdot}5 \times 10^{-4}\%$ RH $+ Co^{2+}$	$-0{\cdot}60$	$-0{\cdot}5$	$-0{\cdot}7$	1×10^{-8}	35
Antimony	$[SbCl_6]^- + R^+ \rightleftharpoons R[SbCl_6] + 2e$; R = Rhodamine C	$1{\cdot}5M$ KCl $+ 0{\cdot}5M$ $H_2SO_4 + 4 \times 10^{-4}M$ R $+ Sb^{(III)}$		$+0{\cdot}8$	$+0{\cdot}35$		36
Iodine	$2I^- + Cl^- + R^+ \rightleftharpoons R[I_2Cl] + 2e$	$0{\cdot}1M$ $H_2SO_4 + 5 \times 10^{-5}M$ R $+ 0{\cdot}1M$ KCl $+ I^-$	$+0{\cdot}55$	$+0{\cdot}8$	$+0{\cdot}35$	5×10^{-9}	37
	$2I^- + SCN^- + (C_2H_5)_4N^+ \rightleftharpoons (C_2H_5)_4N[I_2SCN]$	$0{\cdot}1M$ $H_2SO_4 + 5 \times 10^{-5}M$ R $+ 0{\cdot}1M$ KSCN $+ I^-$		$+0{\cdot}55$	$+0{\cdot}4$		
Nickel	$Ni(DH)_n + 2OH^- \rightleftharpoons NiODH + e$; H_2D = dimethylglyoxime	$0{\cdot}03M$ KOH $+ 1 \times 10^{-6}M$ $H_2D + Ni^{2+}$		$+0{\cdot}8$	$+0{\cdot}4$	2×10^{-9}	38

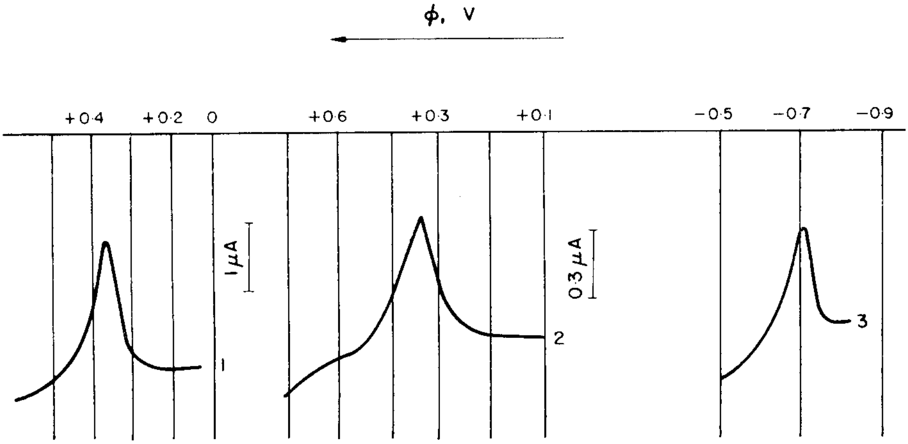

FIG. 4.—Stripping voltammograms of the compounds formed on the graphite electrode from the solutions given below.
1. 0·5*M* $(NH_4)_2SO_4$ + NH_4OH (pH 7) + 4 × 10^{-6} *M* Tl_2SO_4; $\tau_1 = 5$ min; $\varphi_{el} = +1{\cdot}0$ V. *2.* 0·1*M* H_2SO_4 + 0·1*M* KCl + 5 × 10^{-6} *M* Rhodamine C. + 5 × 10^{-7} *M* KI; $\tau_1 = 10$ min; $\varphi_{el} = +0{\cdot}8$ V. *3.* 0·4*M* NH_4OH + 0·05*M* NH_4Cl + 2 × 10^{-6} *M* 2-nitroso-1-naphthol + 4 × 10^{-8} *M* $CoSO_4$; $\tau_1 = 20$ min; $\varphi_{el} = -0{\cdot}5$V.

As an example, Fig. 4 shows voltammograms for thallium(III) hydroxide,[31] iodine chloro-complex with Rhodamine C[37] and cobalt with 2-nitroso-1-naphthol.[35]

It should be noted that the high selectivity of the method under discussion depends on the selectivity of the precipitants used. No ion can interfere with the determination if it does not form insoluble compounds in the test solution and is electrically inactive over the working potential range. Several cases are possible in the presence of other ions capable of varying their oxidation state by electrochemical reaction. If concentration occurs by a reduction reaction the determination cannot be disturbed by dissolved impurities in their lowest oxidation state, and for anodic processes there is no interference from more electropositive species, since the potential will be insufficient to oxidize them. For example, the rare earth elements do not interfere in the determination of cerium, as they are electrically inactive in the potential range from +0·3 to +1·0 V *vs.* S.C.E., over which cerium ion oxidation–reduction occurs[29]; hardly any ions interfere with the determination of iodide, and even large amounts of chloride and bromide may be present.[37]

If an electroactive ion in its original oxidation state forms a sparingly soluble compound with a solution component, in the electrode process which is the reverse of that leading to concentration, there is a possibility of the appearance of a new solid phase. For example, reduction of iron(III) hydroxide results in formation of iron(II) hydroxide on the electrode and this is capable of oxidation during anodic electrode polarization. In such cases the maxima of both cathodic and anodic currents are present on cyclic voltammograms.[39] A similar phenomenon is observed for the system nickel–dimethylglyoxime.[38]

Table VII summarizes the analytical applications of these reactions.

FILM STRIPPING VOLTAMMETRY FOR ANIONS

This variant of the method consists in forming (on the electrode surface) a film of a sparingly soluble compound of the test anions with ions of the electrode material

TABLE VII.—ANALYTICAL APPLICATION OF FILM STRIPPING VOLTAMMETRY FOR VARIABLE VALENCE IONS

Test compound	Test element	Stripping method	Electrode type	Indifferent electrolyte	Sensitivity		Ref.
					M	% *w*/*w*	
Compounds of rare earth elements	Ce(III)	LS	Graphite (ED-6)	MeCl$_3$* + 0·1*M* CH$_3$COONa + 0·1*M* CH$_3$COOH		4 × 10^{-5} – 1 × 10^{-3}	29
PbMoO$_4$,† (NH$_4$)$_2$MoO$_4$,§ Na$_2$WO$_4$¶	Cr(VI)	LS	Graphite (ED-6)	2·5*M* NaOH + 0·2*M* Na$_2$H$_2$EDTA + HNO$_3$, pH 8	1 × 10^{-6}	1 × 10^{-4}	30, 40
				1*M* NaOH + HNO$_3$, pH 8	1 × 10^{-6}	1 × 10^{-4}	
CuSO$_4$	Tl(I)	LS	Graphite (ED-6)	0·5*M* CuSO$_4$ + 0·5*M* (NH$_4$)$_2$SO$_4$ + NH$_4$OH, pH 8	2 × 10^{-6}	7 × 10^{-4}	31
CdSO$_4$	Tl(I)	LS	Graphite (ED-6)	2*M* CdSO$_4$ + 2·5*M* (NH$_4$)$_2$SO$_4$ + NH$_4$OH, pH 8·5	2 × 10^{-6}	1 × 10^{-4}	31
CdSO$_4$	Mn(II)	LS	Graphite (ED-6)	2*M* CdSO$_4$ + NH$_4$OH, pH 5	5 × 10^{-7}	2·5 × 10^{-5}	27
HClO$_4$	Mn(II)	LS	Pt	0·1*M* HClO$_4$	1 × 10^{-7}		26
KCl	Sb(III)	LS	Graphite (ED-6)	2·5*M* KCl + 4 × 10^{-4}*M* Rod.C‡	2 × 10^{-8}	3 × 10^{-6}	36
KCl	I$^-$	LS	Graphite (ED-6)	1*M* KCl + 6 × 10^{-5}*M* Rod.C‡ + 0·1*M* H$_2$SO$_4$ + 5 × 10^{-3}*M* N$_2$H$_4$	6 × 10^{-9}	2 × 10^{-6}	37
Sea-water	I$^-$	LS	Graphite (ED-6)	Sea-water + 5 × 10^{-3}*M* N$_2$H$_4$ + 6 × 10^{-5}*M* Rod.C‡ + 0·2*M* HCl		1 × 10^{-7}	37
Al(NO$_3$)$_3$	Ni(II)	LS	Graphite (ED-6)	0·15*M* Al(NO$_3$)$_3$ + 0·5*M* KOH + 5 × 10^{-6}*M* H$_2$D‖	5 × 10^{-9}	3 × 10^{-6}	

TABLE VII (*Cont.*)

Test compound	Test element	Stripping method	Electrode type	Indifferent electrolyte	Sensitivity		Ref.
					M	% w/w	
$CaCl_2$	Co(II)	LS	Graphite (ED-6)	$1M\,CaCl_2 + 0{\cdot}1M\,NH_4Cl + NH_4OH + 2 \times 10^{-4}M$ R,** pH 8	2×10^{-8}	1×10^{-6}	
$(Er, Y, Nd)_2(MoO_4)_3$††	Co(II)	LS	Graphite (ED-6)	$0{\cdot}25M\,H_3Cit$ + NaOH (pH 8) $+ 0{\cdot}4M\,NH_4OH + 0{\cdot}05M\,NH_4Cl + 2 \times 10^{-6}M$ R**	1×10^{-8}	3×10^{-5}	
Na_2WO_4†§	Ni(II)	LS	Graphite (ED-6)	$0{\cdot}2M\,KOH + 1 \times 10^{-5}M\,H_2D$‖	1×10^{-7}	1×10^{-5}	
H_3Cit	Co(II)	LS	Graphite (ED-6)	$0{\cdot}5M\,Na_3Cit + NaOH + 2 \times 10^{-6}M$ R** pH 10–11	1×10^{-7}	1×10^{-5}	
H_2Tart	Co(II)	LS	Graphite (ED-6)	$0{\cdot}5M\,Na_2Tart + NaOH + 2 \times 10^{-6}M$ R**, pH 9	1×10^{-7}	1×10^{-5}	
H_3Cit and H_2Tart§	Ni(II)	LS	Graphite (ED-6)	$0{\cdot}1M\,NaOH + 1 \times 10^{-5}\,H_2D$‖	2×10^{-7}	1×10^{-5}	

* Test compound metal ion—Me^{n+}.
† Dissolved in NaOH.
‡ Rod. C—Rhodamine C.
§ The substance is heated and dissolved in the indifferent electrolyte.
‖ H_2D—dimethylglyoxime.
¶ The sample is dissolved in 10% NaOH solution, then neutralized with HNO_3.
** R – 2-nitroso-1-naphthol.
†† Dissolved in HCl.

by anodic polarization, followed by cathodic stripping of the film thus formed. The electrode reactions are:[23]

$$M \rightleftharpoons M^+ + e$$

$$M^+ + A^- \rightleftharpoons MA \downarrow$$

where M is the electrode metal, A^- is the anion removed from the solution (assumed for simplicity to be singly charged), and MA is the sparingly soluble compound forming the film on the electrode.

Ball, Manning and Menis[42] were the first to determine chloride ion after its preconcentration in the form of calomel.

A coulometric variation for the determination of chloride or iodide, based on precipitation as the silver halides, has been described by Shain and Perone,[43] who neither predicted the potentialities of the method nor interpreted the results theoretically, which, probably, has groundlessly caused them to give up utilization of a mercury electrode for the determination of iodine ions, since mercury becomes passive in the medium studied.

Brainina[4] has given theoretical consideration to a particular case of irreversible film dissolution. Since in the process of electrodissolving a compound localized on the electrode surface the metal ions being reduced come into contact with the electrode surface, the case may be regarded mathematically as analogous to dissolving the metal from the inert electrode surface. Then, taking into account the results from the papers mentioned[5–8] the relationships may be written (see Table VIII) for parameters of electrodissolution of a compound from the electrically active electrode surface. The amount of material deposited is dependent on the anion concentration and deposition time, and is described by equations similar to (6) and (7).

Since the test substance does not take a direct part in the electrode process, the method may be used to determine electrically inactive substances. Figure 5 shows the voltammograms for some mercury compounds formed from the appropriate anions. Deposition potentials for the mercury salts and approximate potentials of the maxima on the voltammograms are shown in Table IX,[44,45] together with the

TABLE VIII.—PRINCIPAL RELATIONSHIPS BETWEEN THE PARAMETERS OF THE PROCESS OF STRIPPING A COMPOUND FROM AN ELECTRICALLY ACTIVE ELECTRODE SURFACE

Irreversible process

$$I_m = \frac{\alpha nF}{RT} VQ_0 \exp\left[\frac{Sk_s a_\infty RT}{\alpha V}\left(\frac{\delta_1 f}{a_\infty' \gamma nFSD\tau_1}\right)^\alpha - 1\right]$$

Reversible process; rotating electrode

$$I_m = \frac{nF}{RT} VQ_0 \exp\left(\frac{RT}{nFV\tau_1} - 1\right)$$

Reversible process; stationary electrode

$$I_m = 0{\cdot}79 \frac{nF}{RT} VQ_0 \exp\left(\frac{\delta_1}{\sqrt{\frac{nF}{RT}DV\tau_1}} - 1\right)$$

Because $RT/nFV\tau_1$, $\delta_1/\tau_1\sqrt{DVnF/RT}$ and $\frac{Sk_s a_\infty RT}{\alpha V}\left(\frac{\delta_1 f}{a_\infty' \gamma nFSD\tau_1}\right)^\alpha$ are all $\ll 1$, the corresponding exponent values approximate to $e^{-1} \sim 0{\cdot}37$.

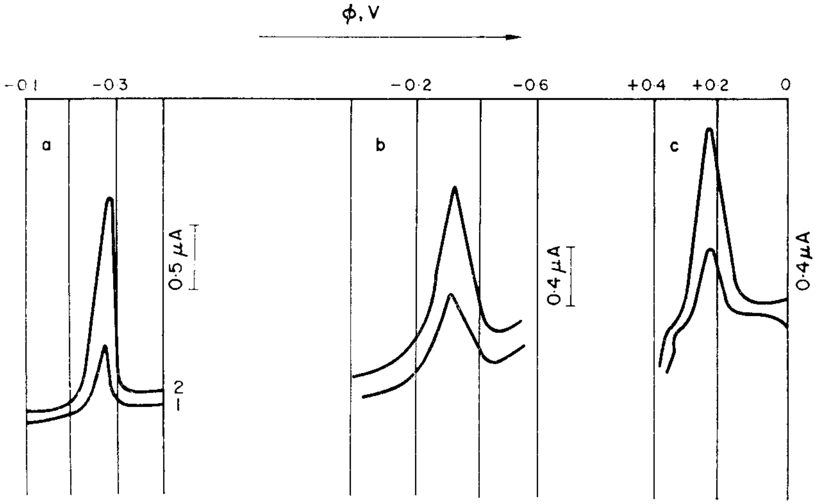

FIG. 5.—Stripping voltammograms of mercury salts deposited on the stationary dropping mercury electrode from the solutions given below.
(*a*) $0{\cdot}06M$ $KNO_3 + 2 \times 10^{-5}$ (*1*) and $4 \times 10^{-5}M$ KI (*2*); $\varphi_{el} = 0{\cdot}1$ V; $\tau_1 = 1$ min.
(*b*) $0{\cdot}1M$ $KNO_3 + 2 \times 10^{-6}$ (*1*) and $4 \times 10^{-6}M$ nickel diethyldithiophosphate (*2*); $\varphi_{el} = 0{\cdot}0$ V.
(*c*) $0{\cdot}05M$ $KNO_3 + HNO_3$ (pH 2) $+ 3 \times 10^{-9}$ (*1*) and $9 \times 10^{-9}M$ K_2CrO_4; $\tau_1 = 10$ min; $\varphi_{el} = +0{\cdot}45$ V.

minimum anion concentrations at which the electrodissolution current for an appropriate salt may be determined with an error not exceeding 20%.

The necessary conditions for forming a film, and the problems of sensitivity and of concentration by absorption have been discussed by Brainina and Roizenblat.[44,45]

Table X shows the scope of the technique. Freischman, Thirsk and others[53–56] have used the method to determine other anions, for example, phosphates. Berge and Jeroschewski[57] have studied the behaviour of sulphur-containing organic

TABLE IX.—CONCENTRATION OF ANIONS IN THE FORM OF MERCURY SALTS

Anion	Indifferent electrolyte	*T*, °*C*	φ_{el}, *V*	φ_m, *V*	$C^0_{1\min}$, *M*
Cl^-	$0{\cdot}1M$ $NaNO_3$	20	+0·35	+0·15	5×10^{-6}
	$0{\cdot}1M$ $NaNO_3$	2			1×10^{-6}
Br^-	$0{\cdot}1M$ $NaNO_2$	20	+0·25	0·0	1×10^{-6}
	$0{\cdot}1M$ $NaNO_2$	2			5×10^{-7}
I^-	$0{\cdot}1M$ $NaNO_2$	20	+0·1	−0·3	5×10^{-8}
S^{2-}	$1M$ NaOH	20	−0·5	−0·9	5×10^{-8}
$CrO_4{}^{2-}$	$0{\cdot}1M$ $NaNO_3$	20		+0·35	3×10^{-9}
$WO_4{}^{2-}$	$0{\cdot}1M$ $NaNO_3$	20	+0·4	+0·25	4×10^{-7}
$MoO_4{}^{2-}$	$0{\cdot}1M$ $NaNO_3$	20	+0·4	+0·20	1×10^{-6}
$VO_3{}^-$	$0{\cdot}1M$ $NaNO_3$	20	+0·4	+0·25	1×10^{-6}
$SO_4{}^{-2}$*		20	−0·5	−0·9	5×10^{-8}
Oxalate	$1M$ KNO_3	20	+0·35	+0·05	1×10^{-6}
Succinate	$1M$ KNO_3	20	+0·40	0·0	1×10^{-4}
Dithizonate	$1M$ KNO_3	20	+0·1	−0·35	1×10^{-5}
Diethyldithiophosphate	$1M$ KNO_3	20	0·0	−0·3	1×10^{-6}

* May be determined only after reduction to S^{2-}, *e.g.*, with titanium(III) in phosphoric acid.

TABLE X.—ANALYTICAL APPLICATION OF FILM STRIPPING VOLTAMMETRY FOR ANIONS

Test compound	Test element	Stripping method	Electrode type	Indifferent electrolyte	Sensitivity		Ref.
					M	%, w/w	
K_2CO_3, Na_2CO_3	SO_4^{2-}*	LS	HMDE (Pt)	$5M$ KOH	5×10^{-8}	5×10^{-6}	46
KNO_3	Cl^-	LS	HMDE (Pt)	$0{\cdot}08M$ KNO_3 + $0{\cdot}002M$ HNO_3	5×10^{-6}		47
$UOSO_4$	Cl^-	LS	Mercury-pool microelectrode	$UOSO_4$ + $0{\cdot}1M$ KNO_3 + $0{\cdot}1M$ H_3Cit	5×10^{-6}		42
$CaWO_4$, $SrWO_4$,† $CaMoO_4$, $SrMoO_4$	Cl^-	LS	HMDE (Pt)	$1{\cdot}2M$ H_2Tart + $0{\cdot}05M$ HNO_3	5×10^{-6}	5×10^{-4}	48
$BaCO_3$, $SrCO_3$, $CaCO_3$	I^-	OP	HMDE (Pt)	$Me(NO_3)_2$	5×10^{-8}	5×10^{-6}	49
$NaNO_3$	I^-				1×10^{-6}		50
$CdSO_4$	CrO_4^{2-}	LS	HMDE (Pt)	$0{\cdot}5M$ $CdSO_4$ + HNO_3, pH 4	2×10^{-9}	2×10^{-7}	51
Water	S^{2-}	LS	HMDE	$0{\cdot}1M$ NaOH	1×10^{-7}	3×10^{-7}	52
CH_3COONa + CH_3COOH	I^-	LS	HMDE	$0{\cdot}1M$ CH_3COONa + $0{\cdot}1M$ CH_3COOH	4×10^{-8}		43
	Cl^-	Coul.		$0{\cdot}1M$ CH_3COONa + $0{\cdot}1M$ CH_3COOH + 80% C_2H_5OH	4×10^{-6}		
$Al(NO_3)_3$	Cl^-	LS	HMDE (Pt)	$0{\cdot}5M$ $Al(NO_3)_3$ + $0{\cdot}08M$ HNO_3 + 80% C_2H_5OH, t° = 2°C	7×10^{-7}	1×10^{-5}	
$Al(NO_3)_3$§	SO_4^{2-}*	LS	HMDE (Pt)	$5M$ KOH + $0{\cdot}5M$ N_2H_4	5×10^{-8}	1×10^{-5}	
KIO_3	I^-	OP	HMDE (Pt)	$0{\cdot}4M$ KIO_3	8×10^{-8}	1×10^{-5}	
KIO_3	S^{2-}‡	LS	Graphite (ED-6)	$0{\cdot}4M$ KIO_3	8×10^{-8}	1×10^{-5}	

* SO_4^{2-} is to be reduced to S^{2-} by titanium(III) phosphate; H_2S is to be absorbed by $5M$ KOH.

† The substances are reduced by zinc amalgam in tartaric acid medium.

§ To be heated.

‡ Indirect method, by excess of mercury in solution which has not reacted.

compounds on a stationary mercury electrode and have demonstrated the possibility of determining microamounts of thiocarbamide ($10^{-8}M$), 2-mercaptobenzothiazole ($10^{-6}M$) *etc.* Hexacyanoferrate(II) ions have been concentrated in the form of a sparingly soluble compound of hexaferrocyanate(III) with mercury and the reduction current for the compound formed has been recorded.

The possibility of concentrating various organic compounds or their decomposition products on the electrode surface facilitates the indirect determination of metal ions, since the interation of the metal ion with the reagent in the solution causes a decrease in the reagent concentration, proportional to the amount of metal ion in solution. Berge and Jeroschewski[58] have made use of the method to determine mercury, platinum, gold and silver indirectly, using thiocarbamide, thionalide, 2-mercaptobenzothiazole and dithio-oxamide. The same authors[59] have determined small amounts of cyanide by forming sparingly soluble CuCN on a stationary mercury electrode.

ELECTRODES IN FILM STRIPPING VOLTAMMETRY

Deposition and dissolution of metals and sparingly soluble compounds of variable oxidation state ions have been accomplished, mainly on solid electrodes of platinum,[3,13,11,60,61,26] gold[62–64] and graphite (carbon). Concentration of iron in the form of $Fe(OH)_3$ on the stationary mercury electrode[39] has been an exception. The development of film stripping voltammetry has depended on the utilization of various types of graphite electrodes which offer rather high hydrogen and oxygen overvoltages (wide working potential range) and possible renewal of the electrode surface simply by removal of the outside layer.

Usually graphite electrodes suffer from a high background current because of reduction of the oxygen either contained in the pores[65] or absorbed,[66] but this shortcoming may be successfully overcome by special preparation of the material to be used.[14,16,36,67–71]

The most generally usable electrodes for film stripping voltammetry are those made of the graphite used for spectroscopy, soaked with epoxy resin and polyethylenepolyamine.[16,36,71] Brainina and co-workers have used these electrodes to investigate the processes of deposition and dissolution of several metals[2] and sparingly soluble compounds.[23,28,33] The determination of many elements has been described, some of which are mentioned in Tables III–VII. Brainina and Beliavskaya have suggested that such electrodes could be used for automated analysis of process solutions.[72]

Perone used a graphite electrode soaked with wax for the deposition and dissolution of silver[14] and mercury.[21] Later Perone and Staplefeldt[15] suggested trying such an electrode in differential film stripping voltammetry. Roizenblat and Brainina have made use of paraffin-soaked electrodes and those soaked with paraffin–polyethylene mixture, in a.c. FSVM.

Recently suggestions have been made for preparing some special graphites, and the properties of non-porous pyrolytic[23,74] and glassy[75–77] graphites described. Vasos and Mark[78] have studied the anodic stripping of thin copper films from pyrolytic graphite electrodes.

An electrode made of carbon paste, suggested by Adams,[79–81] is another variety of the carbon electrode. The paste is a mixture of powdered carbon with an organic liquid which is non-volatile and immixable with water. Olson and Adams[82] have investigated electroreduction and dissolution of a series of metals on these electrodes. Jacobs[22] has obtained voltammograms for the dissolution of gold and silver deposited on similar electrodes.

Farsang and Tomcsányi have studied the oxidation of Mn^{2+} and the reduction of MnO_2 on a carbon-paste electrode.[41] Monen, Specker and Zinke[13] have carried out a comparative investigation of various carbon electrodes: glassy, pyrolytic, spectral, wax-soaked and carbon-paste, with the determination of silver (1–100 ng/ml) in 0·2*M* potassium nitrate solution as an example. They have obtained reproducible results by using carbon-paste and wax-soaked electrodes, the surface of the latter being removed after each measurement. The amount of silver deposited on the pyrolytic and glassy electrodes decreased in repeated measurements. This effect is thought to be due to absorption phenomena or a decrease in the number of active centres on the electrode surface.

Unfortunately, these investigations cannot be regarded as sufficient, and there is a considerable lack of information in the literature concerning the utilization of these electrodes. The graphite electrode soaked with epoxy resin and polyethylenepolyamine seems to receive the most attention. Judging from the results in the papers cited this electrode has high potentialities, providing quite reproducible results.

During recent years an analogy has been drawn between FSVM and amalgam stripping voltammetry[83] because so-called film electrodes (solid electrodes with mercury film) are used in both. The amalgamated electrodes may be considered as a variety of such electrodes, *e.g.*, the amalgamated silver electrode used by Igolinski.[84] In the strict sense of the word, however, the term film electrodes should be reserved for those which consist of a material insoluble in mercury and on which an intermediate layer of amalgam with changeable thickness is not formed.

Moros[85] has suggested a mercury film electrode, made of platinum with a layer of mercury, for the determination of lead chloride, or iodide. A similar electrode has been utilized by Ramaley and others.[86] Roe and Toni[87] have deduced the equation describing the curves for metal dissolution from the mercury film electrode and experimentally confirmed their conclusions, using the amalgamated nickel electrode.

Matson, Roe and Carriet[88] have described a mercury–graphite electrode for anodic voltammetry. They made use of graphite soaked with paraffin in vacuum. The surface of the electrode was polished and then polarized in 5×10^{-8}–$10^{-7}M$ mercury(II) at a potential of −200 mV *vs.* S.C.E. for 10 min. Investigation by microscopy indicated that about 10% of the mercury is on the surface in the form of drops 0·01 mm in diameter, and the rest in the form of smaller drops.

Perone and co-workers have utilized graphite electrodes covered with mercury in many variants of FSV and chronopotentiometry.[89,90]

Roizenblat and Brainina[91] have suggested obtaining such electrodes simply by concentrating the metal after addition of a certain amount of mercury oxynitrate. The mercury–graphite electrode is quite good for the cases where metals deposited during concentration form solid solutions of intermetallic compounds.[91] The presence of mercury weakens metal–metal interactions and reduces the usual difficulties in simultaneous determination of several metals.

Being inert towards the electrode process under consideration, the electrodes described above are suitable for film stripping voltammetry of metals and variable valence ions. For the third variant, *i.e.*, film stripping voltammetry for anions, electroactive electrodes are usable: silver[43] and stationary mercury electrodes.[46–52,57,58] As the latter are well known, no consideration will be given to them here.

SELECTION OF CONDITIONS FOR ANALYSIS

The process of determining a concentration in solution involves the following three stages: (*1*) precipitation, (*2*) equilibration period, (*3*) stripping period.

1. Electrode potential is the main parameter for the first stage. It is chosen in the region corresponding to limiting diffusion current for the ions being concentrated. Then, if the solution is uniformly agitated, the amount of film formed on the electrode is directly proportional to the concentration of the ions involved in the process and to the electrolysis time. Optimal potentials for precipitation of metals and compounds are shown in Tables III, V, VI and IX. If concentrations are to be determined for several metals simultaneously the electrolysis potential is chosen in the region corresponding to limiting diffusion current for the most electronegative metal. Shift of the electrolysis potential to a more negative value does not affect the character of the voltammogram if it still corresponds to the limiting current. Reduction of antimony(III) is an exception, as in this case there is a potential range over which concentration of antimony becomes slower,[92] probably because of inhibition of the cathodic process as the sign of the change on the electrode surface changes. A similar effect may be observed in other cases, as, *e.g.*, with indium(III).[93]

2. During the equilibration the potential is held at the electrolysis potential or at a slightly more positive potential to decrease the background reduction current and that from dissolution of more electronegative species.

3. The stripping process is accomplished in different ways. The most widely used is linear scan of the potential and fixation relation of the current to the electrode potential or time. Either maximum current (anodic or cathodic, depending upon the nature of the electrode reaction) or quantity of electricity is measured. The dependence of these values on concentration of dissolved ions participating in the process has been discussed in detail earlier in the theoretical part of the paper.

It is important to choose the proper rate of change of electrode potential. On the one hand increasing the scan rate is reasonable since the maximum current is directly proportional to this value; in this case, however, the double-layer charging current grows, which interferes with measurements, and decreases the resolving power of the method. For many cases a scan rate of 0·01–0·2 V/sec is optimal.

Sometimes stripping is accomplished at a linearly varying potential with a variable component overlapping[71] and the alternating current amplitude is measured.

Generally speaking, for accomplishment of this stage in FSV it is possible to make use of all the means which are utilized in anodic stripping voltammetry with a mercury electrode: potential step method (chronoamperometry), current step method (chronopotentiometry), chemical stripping, stripping at constant potential followed by reduction (or oxidation) with linear-potential sweep, *etc.* Since the methods are discussed in detail by Barendrecht,[1] there is no point in dwelling on them here, especially as their use in FSV is incidental to the main purpose of this review.

PRACTICAL CONSIDERATIONS

Preparation of electrodes

Graphite electrodes soaked with epoxy resin. Heat 10–15 g of epoxy resin and mix with an equal volume of acetone, then admix 0·2 ml of polyethylenepolyamine.

Heat the mixture to remove acetone and then use it to soak graphite rods turned from spectroscopic carbon (10–15 mm long, 2 mm diameter). Soaking is done in vacuum, with heating for 6 hr. Let the soaked rods stand in air till the resin is completely hardened. Insert each rod into a glass tube, put polyethylene powder on its side surface and melt it down. Repeat the operation 4 or 5 times. Electrical contact is made by mercury or carbon powder.

Electrodes soaked with paraffin and polyethylene. Add small portions of low-pressure polyethylene powder to melted paraffin until 25–30% w/w is present. Soak graphite rods (10–15 mm long, 2 mm diameter) in this mixture in vacuum for 6–8 hr. Use a similar method with paraffin.

Pyrolytic and glassy graphites. Readily used for making electrodes without special preparation.

Carbon-paste electrodes. Mix 50 g of carbon powder and 20 ml of Nujol, and press a small amount of the paste into a glass tube.[81]

Difficulties

Stability of electrode operation and correctness of the results are determined, mainly, by the purity of the solutions and the interaction of precipitates on the electrode.

Good reproducibility is achieved either by removing admixtures of surface-active substances from solutions or periodically renewing the electrode surface. For renewing, various different mechanical cleaning methods are used, *e.g.*, cutting off the outer graphite layer or use of an abrasive. The latter method has opened up for Brainina and Beliavskaya[72] the possibility of extended use of the FSVM method in automated analysis of process solutions containing large amounts of surface-active substances.

Interaction between precipitates on the electrode is manifested in formation of solid solutions and intermetallic compounds. In such cases it is advisable to make use of the mercury film electrodes.[91] The electrode may be coated with the film beforehand or simultaneously with the precipitation of the metal.

Preparation of the electrodes as described gives results reproducible within 10–15% for determinations at the 10^{-8}–$10^{-7}M$ level.

Ohmic drop distortion in solution and the electrode potential result in distortion of potential scan linearity, particularly in dissolution of thick films. This distorts the voltammograms and decreases the maximum current. The difficulty is eliminated by using apparatus equipped with special compensators for ohmic drop and with a three-electrode cell. Most polarographs produced nowadays enable this difficult to be overcome.

Sometimes difficulties may arise from slow formation of electroactive complexes, *e.g.*, reaction between nickel and dimethylglyoxime continues for 30 or 40 min. In this case it is necessary to prepare the analytical solutions beforehand.

CONCLUSION

It can be concluded that the FSV method which has been developed in recent years is a highly useful method of wide applicability.

The possibility of identifying variable valence ions, anions, organic compounds, noble metal ions and those of metals unable either to form amalgams or to be reduced to the elementary state makes the method much more widely applicable than the variants of film voltammetry described earlier.[1,83,95]

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Zusammenfassung—Die inverse Film-Voltammetrie ist ein neues elektrochemisches Analysenverfahren. Die zu bestimmende Substanz wird als Metall oder schwerlösliche Verbindung auf der Elektrodenoberfläche abgeschieden und dann der Strom zur Wiederauflösung des Niederschlags registriert. Das Verfahren wurde zur Bestimmung von Metallionen, Anionen und Ionen mit verschiedenen Valenzen bei Empfindlichkeiten bis herunter zu $10^{-9}M$ ausgearbeitet. Als Indikatorelektroden werden feste, im allgemeinen Graphitelektroden, sowie stationäre Quecksilberelektroden verwendet.

Résumé—La voltammétrie de dissolution de film est une nouvelle méthode analytique électrochimique consistant à concentrer la substance à l'essai sous la forme d'un métal ou d'un composé faiblement soluble à la surface de l'électrode, puis à enregistrer le courant nécessaire à l'électrodissolution du dépôt. La méthode a été élaborée pour la détermination d'ions métalliques, d'anions et d'ions de valence variable, avec des sensibilités allant jusqu'à $10^{-9}M$. Comme électrodes indicatrices, on utilise des électrodes solides, habituellement en graphite, et des électrodes de mercure stationnaires.

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ANION-EXCHANGE SEPARATIONS OF METAL IONS IN THIOCYANATE MEDIA*

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Summary—The analytical potential of a weak-base macroreticular anion-exchange resin for the quantitative separation of metal ions in thiocyanate media is investigated and demonstrated. Distribution data are given for the sorption of some 25 metal ions from aqueous mixtures of potassium thiocyanate (1.0*M* or less) and 0.5*M* hydrochloric acid. The magnitude of the distribution data suggests many possible separations, some of which were quantitatively performed by procedures which are fast, simple and require only mild conditions. Representative separations are removal of traces of iron(III) and copper(II) from water samples prior to the determination of water hardness (calcium and magnesium), separation of nickel(II) from vanadium(IV) and the separation of thorium(IV) from titanium(IV). Some multicomponent separations are the separation of rare earths(III) and thorium(IV) from scandium(III) and the separation of rare earths(III) from iron(III) and uranium(VI).

MUCH information has been reported on the anion-exchange behaviour of metals in a number of different media. Kraus and Nelson[1] reported the behaviour of most metals in the periodic table over a broad range of hydrochloric acid concentrations. Their anion-exchange work, and indeed much of the similar work reported in the literature involves the use of strong-base resins.

The purpose of this work is to investigate systematically the analytical potential of a macroreticular weak-base anion-exchange resin (Rohm and Haas Amberlyst A-21) for the quantitative separation of metal ions in thiocyanate media. Thiocyanate was the ligand of choice because it forms complexes with numerous metal ions[2,3] and its potential in weak-base systems has not been thoroughly investigated. The only work reported on the application of weak-base anion-exchange resins for the selective sorption of metal ions from thiocyanate media is a series of papers by Kuroda and co-workers[4,5,6] and Hamaguchi *et al.*,[7] who used the weakly basic anion-exchanger diethylaminoethyl (DEAE) cellulose.

EXPERIMENTAL

Ion-exchange resin and columns

Amberlyst A-21 is a macroreticular weak-base anion-exchange resin in the -$N(CH_3)_2$ form. It was obtained as a free sample from Rohm and Haas Company in the form of 20–50 mesh hard insoluble beads which were ground and sieved to yield an 80–100 mesh cut. The resin was washed with methanol and air-dried before use. The resin was packed into the column with water before being converted into its thiocyanate form by washing with a solution 1·0*M* in potassium thiocyanate and 0·5*M* in hydrochloric acid. The capacity of the resin was determined by the Volhard method[8] to be 3·25 meq/g. The columns used for separations were 10 × 90 mm or shorter, or 20 × 90 mm.

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Metal ion solutions and eluents

Stock solutions. In almost all cases the reagent grade chloride, nitrate, or oxide of the metal ion was used and diluted to a final acid concentration of 0·5*N* unless hydrolysis was a problem. Titanium(IV) solution was prepared by dissolving an appropriate aliquot of titanium tetrachloride in concentrated hydrochloric acid and then carefully diluting with distilled water.

Sample preparations. Synthetic sample mixtures for column separation studies were prepared by mixing given volumes of standardized metal ion solutions and eluent. Concentration ranges were adjusted so that the sample volume added to the column was either 1 or at most 2 ml.

Eluents. The eluents used for column separations were acidic solutions of potassium or ammonium thiocyanate. Eluents were prepared immediately before use by mixing equal volumes of hydrochloric acid and potassium or ammonium thiocyanate of appropriate molarity.

Analytical determinations

Qualitative spot tests on column effluents were performed with Arsenazo I buffered with pyridine. Quantitative determinations were accomplished *via* EDTA titrations.

Batch distribution ratios

Two g of dry equilibrated resin were added to 125-ml Erlenmeyer flasks containing a metal ion solution (0·1–0·2 mmole) at the appropriate thiocyanate concentration. The flasks were automatically shaken for 30 min and aliquots of the aqueous phase taken and analysed. The amount of metal ion retained by the resin was determined by material balance.

RESULTS

Batch distribution ratios were determined for a number of metal ions at thiocyanate concentrations ranging from 0·03 to 1·0*M*. Log-log plots of distribution ratio *vs.* thiocyanate concentration for several metals are given in Figs. 1 and 2. The following metals had distribution ratios $\geqslant 1000$ from 0·03*M* thiocyanate solution: bismuth(III), cadmium(II), cobalt(II), copper(II), indium(III), iron(III), mercury(II), molybdenum(VI), uranium(VI), vanadium(IV), and zinc(II).

A study of distribution ratio *vs.* shaking time was performed for the uptake of scandium(III) from two different thiocyanate concentrations. A plot of D/D_{eq} in Fig. 3 indicates that equilibrium is attained within 3 min for 0·35*M* thiocyanate and within 5 min for 0·70*M* thiocyanate.

A study of the rate of desorption of scandium(III) from A-21 resin was performed in the following manner. Scandium(III) was extracted from 1·0*M* potassium thiocyanate–0·5*M* hydrochloric acid into 2·0-g samples of resin. The amount of metal ion sorbed was determined by difference after titration of an aliquot of the aqueous phase. Then the scandium(III) was back-extracted from the resin samples, various shaking times being used. The solution used for back-extraction was 0·02*M* potassium thiocyanate–0·5*M* hydrochloric acid. The distribution ratio for the direct extraction of scandium(III) into A-21 from this solution was nil. However, equilibrium for the back-extraction was attained after 1·5 min shaking, with only 80% of the scandium(III) being back-extracted. This corresponds to a distribution ratio of 0·25 for the direct extraction.

Previous work showed that iron(III) and several other metallic elements are difficult to remove from anion-exchange resins of the quaternary ammonium type.[11,12] However, we found that metal ions may be eluted from the tertiary amine type of anion-exchanger with aqueous perchloric acid–thiocyanate mixtures or with hydrochloric acid in acetone. Perchlorate is strongly sorbed by the resin and thus will displace thiocyanate fairly efficiently. Hydrochloric acid in acetone appears to convert metal thiocyanate complexes into metal chloride complexes. The chloride complexes may be displaced from the column by water or dilute aqueous hydrochloric

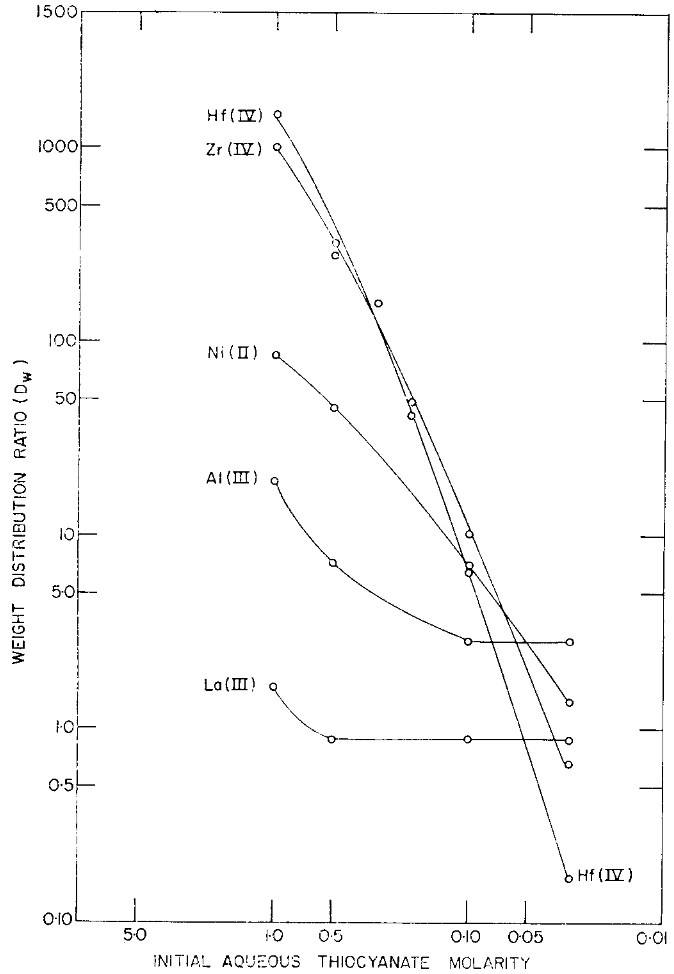

FIG. 1.—Distribution data for the sorption of metal ions from aqueous thiocyanate–0·5M HCl into Amberlyst A-21 resin.

acid. The following elements were quantitatively eluted from a 10 × 90 mm A-21 column by 30–40 ml of 1·0M perchloric acid (or sodium perchlorate)–0·01M ammonium thiocyanate at a flow-rate of 1 ml/min: bismuth(III), cadmium(II), cobalt(II), indium(III), vanadium(IV), uranium(VI), and zinc(II). Iron(III) was eluted from the same column by 30 ml of acetone–hydrochloric acid–water (25:2:2) at a flow rate of 1–5 ml/min.

The removal of iron(III) and copper(II) from water prior to a hardness titration was used to demonstrate the practicality of rapid, quantitative group separations on an A-21 column. Traces of dissolved iron, copper and several other metal ions may interfere with water hardness titrations by combining with the indicator and reducing the sharpness of the end-point or even by blocking the indicator completely so that no colour change occurs. Cyanide masks these metals if their concentration is not too great, but its use is hazardous.

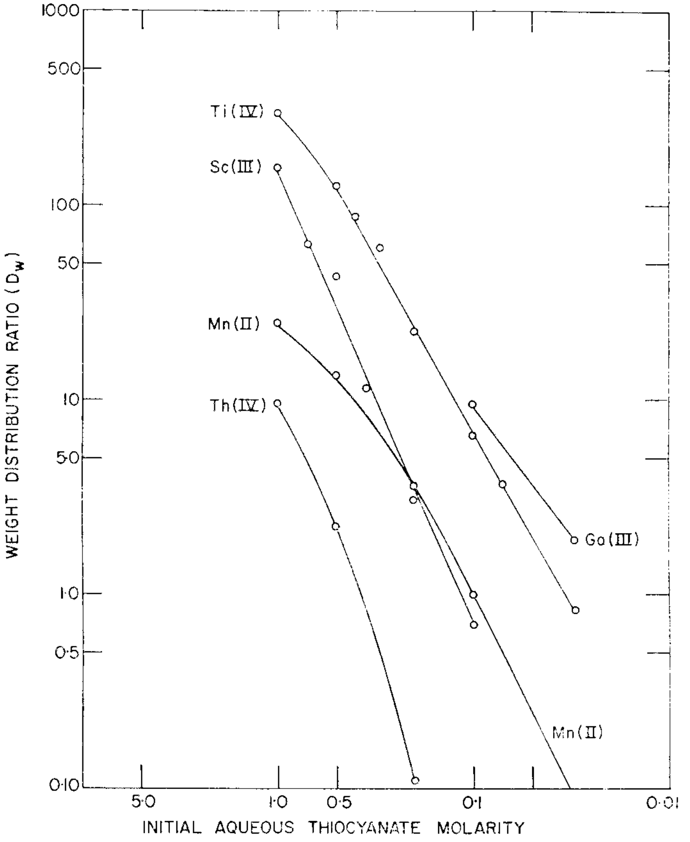

FIG. 2.—Distribution data for the sorption of metal ions from aqueous thiocyanate–0·5M HCl into Amberlyst A-21 resin.

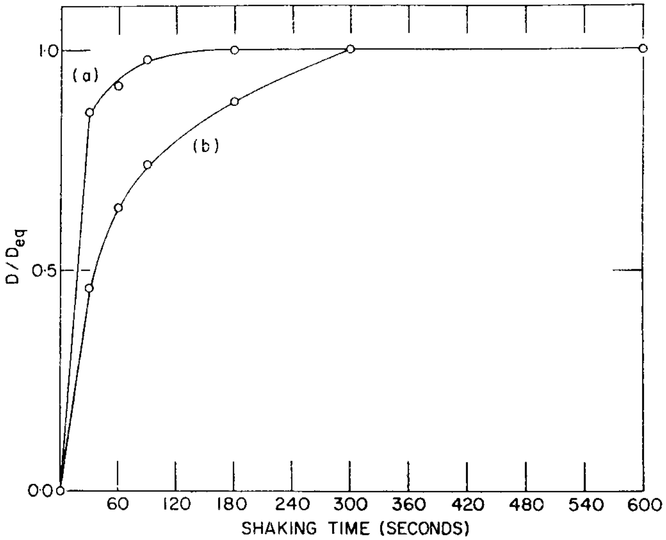

FIG. 3.—Rate of sorption of Sc(III) from aqueous thiocyanate solution into Amberylst A-21 resin. Solution (*a*) is 0·35M KSCN–0·5M HCl and (*b*) is 0·70M KSCN–0·5M HCl.

A 20 × 90 mm column of A-21 resin in the thiocyanate form was used to remove iron(III) and copper(II). A sample of city water containing 20 ppm of added iron(III) and 10 ppm of added copper(II) was made 0·01M in hydrochloric acid and 0·01M in ammonium thiocyanate. A 1-l. sample was continuously passed through the column and various fractions were collected and titrated for hardness by the method of Fritz, Sickafoose and Schmitt.[9] The effluent was clear and all titration end-points were excellent. The coloured iron and copper bands were visible on the top 40 mm of the column. Titration results are given in Table I. The flow-rates were very fast and the capacity of the column is sufficient for many samples.

TABLE I.—DETERMINATION OF TOTAL HARDNESS IN AMES, IOWA, WATER AFTER REMOVAL OF ADDED 20 PPM OF IRON(III) AND 10 PPM OF COPPER(II)

Fraction of effluent collected, *ml*	Flow-rate, *ml/min*	Volume titrated, *ml*	Ca + Mg recovery, % (initially 93·0 ppm)
50–100	10·9	50	100·0
150–200	11·1	50	100·2
250–350	—	100	100·2
450–500	—	50	100·0
600–700	9·5	100	100·4
850–900	—	50	100·2

Many other separation possibilities are suggested by the data on distribution ratios. The separation of scandium(III) from thorium(IV) and rare earths(III) was investigated quantitatively. Preliminary studies using spot tests for the individual metal ions indicated that the separation could be accomplished on a 10 × 90 mm column of A-21. The elution curve for the separation of 0·01 mmole of lanthanum(III), and 0·02 mmole of thorium(IV) from 0·02 mmole of scandium(III) is shown in Fig. 4. For two such separations the recovery of scandium(III) was 100·5% and 100·0% respectively. This separation was qualitatively confirmed with dysprosium(II) or lutetium(III) in place of lanthanum(III). This method is a simple, rapid and convenient way to separate scandium on a short column.

Other separations accomplished on a 10 × 90 mm column are listed in Table II. The elution curve for the nickel(II)–vanadium(IV) separation is shown in Fig. 5, and the thorium(IV)–titanium(IV) separation is equally as good. The flow-rates used for these separations were controlled at 1·0 ml/min.

A shorter column and faster flow-rate should be applicable for separations involving metal ions with very low distribution ratios (such as nickel or rare earths) and ions with distribution ratios above 1000 [such as vanadium(IV), iron(III) and uranium(VI)]. The separation of rare earth (dysprosium) from iron and uranium was repeated on a shorter (10 × 50 mm) column. Dysprosium was eluted with 15 ml of 0·5M potassium thiocyanate–0·5M hydrochloric acid and iron and uranium were stripped with 13 ml of acetone–water-hydrochloric acid (25:2:2). The total time from addition of the 1·0 ml-sample to completion of stripping of iron and uranium was 5 min (*i.e.*, an average flow-rate of 5·8 ml/min). The iron and uranium bands were still located at the top 10–20 mm of the column until they were stripped. The recovery of dysprosium was 100·0% while the recovery of iron was 99·5%.

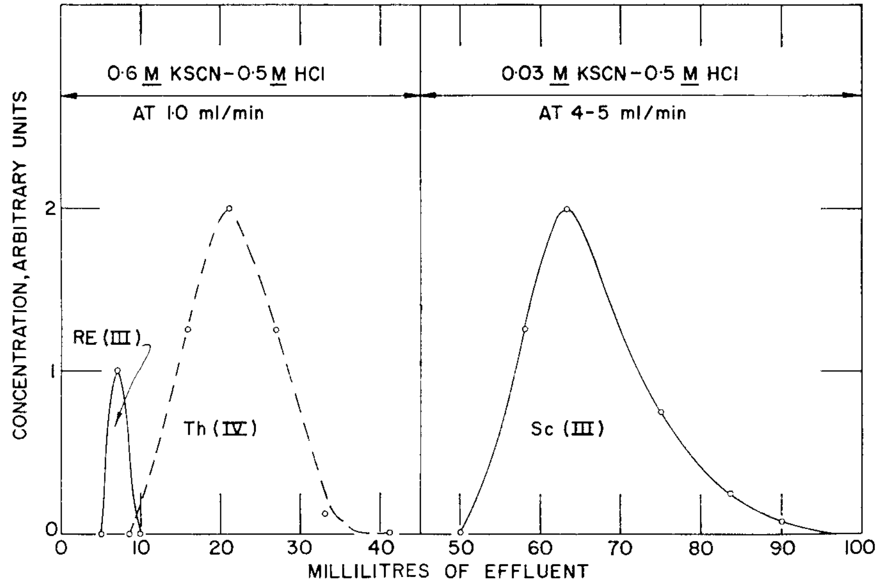

FIG. 4.—Elution curve for the separation of 0·01 mmole of rare earth(III) and 0·02 mmole of Th(IV) from 0·02 mmole of Sc(III).

TABLE II.—SEPARATIONS ON A 10 × 90 mm COLUMN OF A-21 RESIN

Sample mixture, *mmole*	Eluent and volume, *ml*	Recovery, %
Ni(II) 0·04	0·045*M* NH_4SCN–0·5*M* HCl, 30	100·0, 100·7, 100·7, 100·0
V(IV) 0·025	1·0*M* $NaClO_4{}^4$—0·01*M* NH_4SCN, 25	— — 99·6, 100·8
La(III), Er(III), Lu(III) 0·01	0·5*M* NH_4SCN–0·5*M* HCl, 20	100·0, 101·0, 100·0
Fe(III) 0·01	Acetone–H_2O–HCl(25:2:2), 25	99·5, 99·5, 99·9 qualitative
Th(IV) 0·02	0·3*M* KSCN–0·5*M* HCl, 35	99·1, 99·6
Ti(IV) 0·02	0·02*M* KSCN–0·5*M* HCl, 40	qualitative

DISCUSSION

The separations investigated here compare favourably in effectiveness and convenience with those reported by other workers who used thiocyanate systems. Also, the weak-base A-21 resin results in significantly different behaviour in some cases from that reported with other types of anion-exchange resins. For example, our separations of thorium(IV) and scandium(III), and rare earth(III) and scandium(III) are considerably faster than those reported by Hamaguchi *et al.*[10] for Dowex-1 X8 in a thiocyanate system. The separations reported by Majumdar and Mitra[11] generally require 150–200-ml fractions for each element eluted. Turner *et al.*[12] surprisingly found no appreciable absorption of uranium(VI) by Dowex-1 X8 at thiocyanate concentrations up to 8*M*. They experienced some difficulty in eluting metals that form thiocyanate complexes from the column.

A weak-base cellulose anion-exchanger investigated by Kuroda *et al.*[4–6] and Hamaguchi *et al.*[7] [dimethylaminoethyl (DEAE) cellulose] showed that only 6 metal ions are strongly sorbed from 0·005–1·0*M* ammonium thiocyanate: rhenium(VII), molybdenum(VI), tungsten(VI), mercury(II), platinum(IV) and palladium(II).

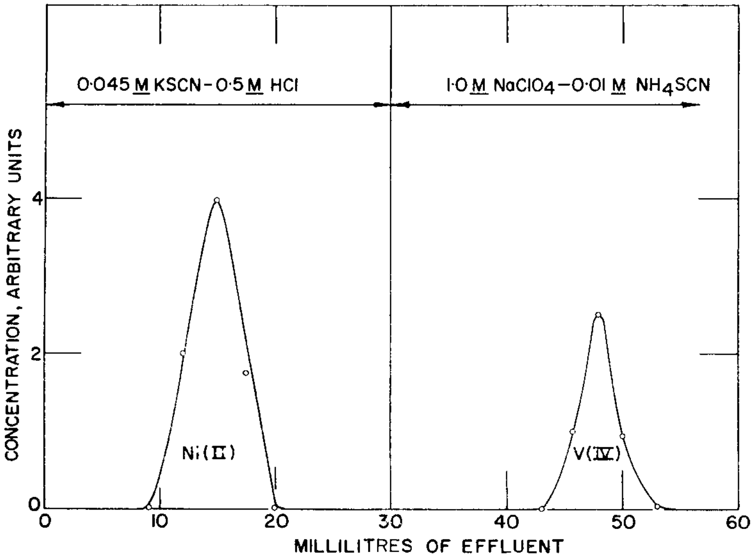

FIG. 5.—Elution curve for the separation of 0·04 mmole of Ni(II) and 0·025 mmole of V(IV).

Other metal ions that are strongly sorbed in the A-21 thiocyanate systems [*e.g.*, iron(III), cobalt(II) and copper(II)] are easily eluted from the cellulose column.

Zusammenfassung—Die analytischen Anwendungsmöglichkeiten von einem schwach basischen, grob vernetzten Anionenaustauschharz für die quantitative Trennung von Metallionen in Thiocyanatmedien werden untersucht und dargestellt. Verteilungsdaten für die Sorption von etwa 25 Metallionen aus wäßrigen Mischungen von Kaliumthiocyanat (1,0*M* oder weniger) und 0,5*M* Salzsäure werden angegeben. Die Größe der Verteilungsdaten legt die Möglichkeit vieler Trennungen nahe; einige davon wurden mit raschen und einfachen Verfahren unter milden Bedingungen ausgeführt. Beispiele sind die Entfernung von Spuren Eisen(III) und Kupfer(II) aus Wasserproben vor der Bestimmung der Wasserhärte (Calcium und Magnesium), die Trennung von Nickel(II) und Vanadium(IV) sowie die Trennung von Thorium(IV) und Titan (IV). Beispiele für Trennungen mehrerer Komponenten sind die Abtrennung der seltenen Erden(III) und Thorium(IV) von Scandium(III) und die Abtrennung der seltenen Erden(III) von Eisen(III) und Uran(VI).

Résumé—On étudie et démontre le potentiel analytique d'une résine échangeuse d'anions macroréticulaire faiblement basique pour la séparation quantitative d'ions métalliques en milieu thiocyanate. On fournit les données de partage pour la sorption de quelques 25 ions métalliques de mélanges aqueux de thiocyanate de potassium (1,0*M* ou moindre) et d'acide chlorhydrique 0,5*M*. L'importance des données de partage suggère de nombreuses séparations possibles, dont quelques-unes ont été réalisées quantitativement par des techniques qui sont rapides, simples et ne nécessitent que des conditions douces. Des séparations caractéristiques sont l'élimination de traces de fer(III) et de cuivre(II) d'échantillons d'eau avant la détermination de la dureté de l'eau (calcium et magnésium), la séparation du nickel(II) du vanadium(IV) et la séparation du thorium(IV) du titane(IV). Quelques séparations comportement de nombreux constituants sont la séparation des terres rares(III) et du thorium(IV) du scandium(III) et la séparation des terres rares(III) du fer(III) et de l'uranium(VI).

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SHORT COMMUNICATION

Chelatbildene Austauscherharze XI*— Abtrennung des Be(II) vom Al(III) am Chelataustauscher auf der Basis von *o*-(2-Hydroxyphenylazo)benzoesäure

(*Eingegangen am* 30. *Juli* 1970. *Angenommen am* 4. *September* 1970)

In mehreren Veröffentlichungen wird die Synthese[1] und die Anwendung[2,3] eines Chelataustauschers auf der Basis von *o*-(2-Hydroxyphenylazo)benzoesäure beschrieben. In einer unlängst erschienenen Arbeit[4] ist eine polarographische Beryllium(II)-Bestimmung in Gegenwart geringer Überschüsse von Aluminium(III) unter Verwendung eines *o*-Hydroxy-*o'*-carboxydisubstituierten Phenylazonaphthalins angegeben. Diese Gruppierung ähnelt der chelatbildenden Ankergruppe des Chelataustauschers.

Ziel einer Untersuchungsreihe ist es, die auffallende unterschiedliche Stabilität der Beryllium(II)- und Aluminium(III)-Chelate für folgende analytische Verfahren auszunutzen:

(*a*) Trennung Beryllium/Aluminium am Chelataustauscher auf Basis *o*-(2-Hydroxyphenylazo)-benzoesäure.

(*b*) Polarographische Bestimmung von Beryllium in Gegenwart von Aluminium unter Verwendung von *o*-(2-Hydroxy-5-methylphenylazo)benzoesäure.

(*c*) Extraktive Trennung Beryllium/Aluminium unter Verwendung von *o*-(2-Hydroxy-5-methylphenylazo)benzoesäure.

Die vorliegende Veröffentlichung behandelt die Trennung Beryllium/Aluminium am Cheltaustauscher. Beryllium wird dabei nach Verfahren (*b*) bestimmt, worüber an anderer Stelle[5] berichtet wird.

Über das Verhalten von Beryllium und Aluminium an Austauschern liegen zahlreiche Untersuchungen vor.[6-8] Verwendet werden im allgemeinen Elutionsmittel, die Komplexbildner enthalten. Oft ist dies ein Nachteil für die Bestimmung der Elemente im Eluat.

Chemikalien

Chelataustauscher: Mit 3 Mol-% Divinylbenzol vernetztes Perlpolymerisat mit *o*-Hydroxy-*o'*-carboxyazogruppen, 100–200 mesh, Kapazität: 3,20 mMol/Gramm lufttrockenem Material.[4] $Be(NO_3)_2 \cdot 4H_2O$ "reinst" und $Al(NO_3)_3 \cdot 9H_2O$ "reinst" (Merck).

Ermittlung der Trennbedingungen

Die pH-abhängige Lage der Verteilungsgleichgewichte wird nach dem Säulendurchlaufverfahreng[9] ermittelt. Verwendet werden Testlösungen von 250 ml Gesamtvolumen. Sie sind 0,25*M* an Kaliumnitrat, 0,0 bis 4,0*M* an Ammoniumacetat und 0,05*M* an Berylliumnitrat bzw. 0,05*M* an Aluminiumnitrat. Die Einstellung entsprechender pH-Werte geschieht durch Zugabe von 0,1*M* Salpetersäure. Die durch Fritten verschlossenen Säulen sind als Doppelwandgefäße an einen Thermostaten (20°) angeschlossen.

Ein Gramm des in der NH_4^+-Form vorliegenden Austauschers wird bei maximaler Tropfgeschwindigkeit mit je 10 ml der entsprechenden Testlösung zwei Mal vorgewaschen und anschließend mit den verbleibenden 230 ml bei einer Tropfgeschwindigkeit von 0,5 ml/min beladen. Anschließend wird mit 50 ml Wasser neutral gewaschen und dann mit 100 ml 2*M* Salzsäure eluiert. In einem aliquoten Teil des auf 250 ml verdünnten Eluats, das nach Zusatz von Kaliumhydroxid einen pH-Wert von 4,0 hat, wird Beryllium(II) mit *o*-(2-Hydroxy-5-methyl-phenylazo)benzoesäure und Aluminium(III) mit Solochromviolett RS[10] polarographisch bestimmt.

Die Polarogramme werden nach der Methode des Standardzusatzes ausgewertet. Mit den erhaltenen Analysenwerten ergeben sich die experimentellen Verteilungskoeffizienten und daraus durch Division die Trennfaktoren. Ihr Logarithmus ist in Abhängigkeit vom pH-Wert in Abb. 1 dargestellt.

Modelltrennung Beryllium/Aluminium

Zur Regelung der Strömungsgeschwindigkeit dient eine Schlauchpumpe (Bühler). Das Eluat volumen (V_E) wird durch Wägung der im Fraktomat "Y 3" (Haiss) aufgefangenen Fraktion bestimmt.

---

* Mitteilung X, Z. Anal. Chem. 1970, 251, 180.

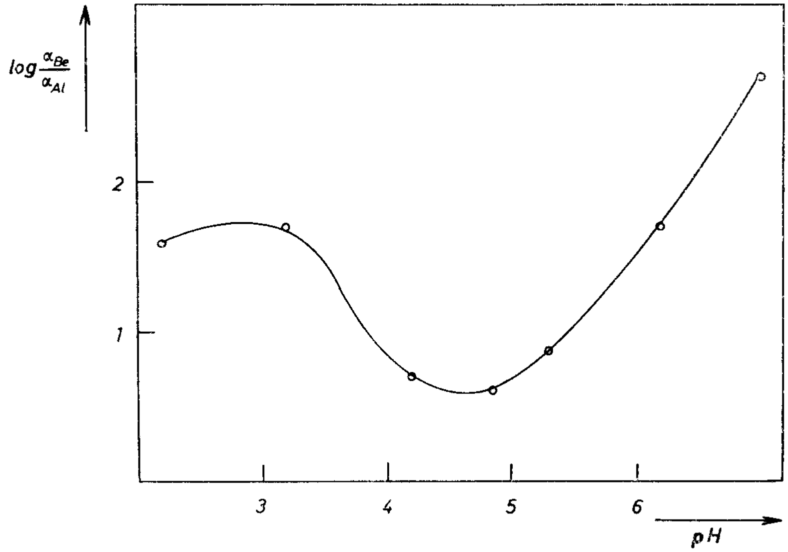

ABB. 1.—Einflüß des pH-Wertes auf $\log \frac{\alpha_{Be}}{\alpha_{Al}}$.

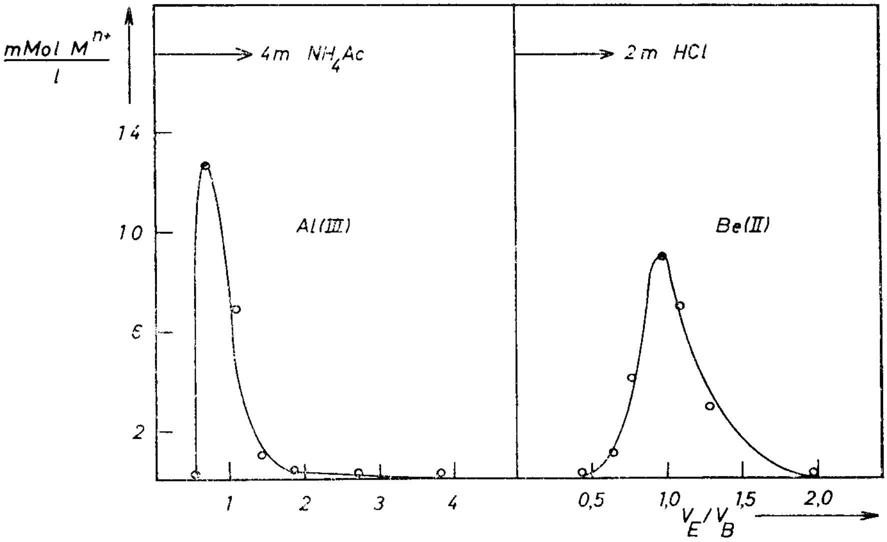

ABB. 2.—Konzentrationsverlauf im Eluat.

Versuchsbedingungen:

Säulenhöhe	0,27 m
Säulenquerschnitt	100 mm^2
Harzmasse	10 g (32 mMol)
Harzbettvolumen	19 ml (V_B)
Beladungsform	NH_4^+, pH 7,0
Elutionsmittel	Al(III): 4,0M NH_4CH_3COO mit 0,1M HNO_3 auf pH 7,0 eingestellt Be(II): 2M HCl
Testlösung	0,243 mMol Be(II) und 0,204 mMol Al(III) in 10 ml 4,0M NH_4CH_3COO-Lösung, pH 7,0
Durchflußgeschwindigkeit	0,5 ml/min

Der Konzentrationsverlauf im Eluat ist in Abb. 2 dargestellt. Aluminium(III) ist unmittelbar nach Ablauf des Zwischenkornvolumens (0,4 V_E/V_B) nachzuweisen. Es wird mit 1,8 V_E/V_B 4M Ammoniumacetatlösung ausgewaschen. Der polarographische Nachweis des Be(II) fällt selbst nach 18 V_E/V_B 4M Ammoniumacetat negativ aus.

Diskussion

Grundsätzlich kann eine Trennung Beryllium/Aluminium im pH-Bereich von 3,0–7,0 vorgenommen werden. Nach Abb. 1 liegen die optimalen Trennbedingungen (Trennfaktor ~500) bei pH 7,0 im 4M Ammoniumacetat. Bei diesem pH ist noch keine Hydrolysefällung bemerkbar. Für eine sichere quantitative Trennung sind jedoch pH-Werte <7 zu empfehlen.

Für die Bereitstellung von Mitten danken wir dem Bundesministerium für Bildung und Wissenschaft.

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Zusammenfassung—Der Chelataustauscher auf Basis *o*-(2-Hydroxyphenylazo)benzoesäure erlaubt die schnelle und quantitative Trennung des Systems Beryllium/Aluminium.

Summary—A chelate-exchanger based on *o*-(2-hydroxyphenylazo)-benzoic acid is used for the rapid and quantitative separation of beryllium from aluminium. Aluminium is eluted with 4M ammonium acetate, and beryllium with 2M hydrochloric acid.

Résumé—On utilise un échangeur de chélate basé sur l'acide *o*-(2-hydroxyphénylazo) benzoïque pour la séparation rapide et quantitative du béryllium de l'aluminium. On élue le l'aluminium à l'acétate d'ammonium 4M et béryllium à l'acide chlorhydrique 2M.

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Talanta, 1971, Vol. 18, pp. 553 to 556. Pergamon Press. Printed in Northern Ireland

ANNOTATION

Design of olfactory detection reactions based on isocyanide formation

(*Received* 11 *June* 1970, *Accepted* 17 *September* 1970)

THIS annotation is meant to provide a convenient source of information on the design of olfactory detection reactions based on isocyanide formation.

Olfaction as a method of detection is rapid, inexpensive, selective and extremely sensitive.[1,2] Olfactory sensing has also been used for physico-chemical measurements, *e.g.*, establishing a pattern of change of gas concentration during flow through an adsorbent bed.[1]

The combination of a chemical reaction with olfactory sensing for detection applications is a conventional principle. The example best known to organic chemists is the reaction of a primary amine, chloroform and alcoholic base to give an isocyanide. This is often used as a method of distinguishing primary amines from secondary and tertiary amines.[3] Another detection reaction based on isocyanide formation is the dehydration of *N*-alkylformamides by electrophilic chemicals.[4]

Recently, odour recognition and odour detection threshold data were obtained for human response to several chemicals, including isocyanides, in order to evaluate critically the use of olfaction as a detection method.[5,6] The results indicate that odour detection thresholds do not vary significantly when the subjects are tested either during the day or the night, in the light or the dark, under auditory stress or under conditions of exercising or resting.

Low odour detection threshold, characteristic odour, and low toxicity are ideal properties for the product of an olfactory detection reaction. Isocyanides have very low odour detection thresholds (in the order of 7ng/l. for methyl isocyanide). The isocyanide odour is "horrible", "extremely distressing" and "highly specific, almost overpowering."[7] It was also cited that with a few exceptions, isocyanides exhibit no appreciable toxicity for mammals.[8] Oral and subcutaneous doses of 500–5000 mg/kg can be tolerated by mice.[8] Therefore, it is logical to consider the detection applications of olfactory sensing of isocyanides produced in chemical reactions.

Table I lists reagent combinations which are known to form isocyanides. Potential detection, warning or identification schemes based on olfactory sensing of isocyanides can be designed by scanning Table I for the specific reagents or classes of compounds to be detected and then tabulating the possible reagent combinations which will produce isocyanides. Preliminary screening and evaluation concerning reaction yields and experimental conditions can be made by examining the original literature references, which are mostly compiled in a recent review.[7] Application of this procedure will vary depending on the nature of specific problems. A chemical method for the detection of isocyanides (lower limit about 0·1 μg) is available for cases in which olfactory sensing is not applicable because of reagent quantity, volatility or toxicity.[9]

TABLE I.—REAGENTS THAT FORM ISOCYANIDES

Reagent		Reagent combination producing isocyanide (Δ = heat)
No.	Name	
1	Acetic anhydride	74 + 1
2	*syn*-Aldoximes	2 + 12 + 83
3	Alkali metal hexacyanocobaltates	Δ + alkylation product of 3 5 + alkylation product of 3 25 or 26 + alkylation product of 3
4	Alkali metal hexacyanoferrates	Δ + alkylation product of 4 5 + alkylation product of 4 25 or 26 + alkylation product of 4
5	Alkali metal hydroxides	—
6	Alkali monoalkyl sulphates	6 + 26
7	Alkyl halides	7 + 26
8	Alkyl iodides	8 + 76 8 + 25
9	Aniline	9 + 80 + Δ
10	*p*-Anisidine	10 + 80 + Δ

TABLE I *continued*

Reagent		Reagent combination producing isocyanide (Δ = heat)
No.	Name	
11	*β*-Arylglycidamides	11 + 46
12	Bases	—
13	Benzenesulphonyl chloride	13 + 75 + 58
		36 + 13 + 73
		13 + 73 + 58
		45 + 13 + 12
		14 + 13 + 12
14	*syn*-Benzilmonoketoxime	14 + 13 + 12
15	Boron trifluoride/mercuric oxide	2 + 56 + 15
16	Tri-n-butylamine	58 + 61 + 16
17	*N*-t-Butyl-1-bromocyclohexanecarboxamide	17 + 69 + Δ
18	1-t-Butyl-2, 2-dimethylaziridine-3-one	18 + Δ
19	t-Butylthioformamide	12 + 19 + 83
20	Carbon tetrachloride	20 + 72 + 24
21	Chlorite	21 + 81
22	Chloroform	72 + 22 + 38
23	*N*-(4-Chlorophenyl)dichloromethylsulphonamide	23 + 79
24	Copper	53 + 24
		20 + 72 + 24
25	Cuprous cyanide	8 + 25
26	Cyanide	26 + 7
		6 + 26
		30 + 26
27	Cyanogen bromide	59 + 27 + 12
28	Cyanuric chloride	70 + 28 + 58
29	*N*-Cyclohexyldichloroacetamide	29 + 69
30	Dialkyl sulphates	30 + 26
31	*N*,*N'*-Diaryl-*N*-hydroxyformamidines	31 + Δ
32	Diazomethane	32 + 40
33	Dichlorocarbene	33 + 68
		33 + 72
34	*N*,*N*-Diethylaniline	58 + 61 + 34
35	*N*,*N*-Dimethylcyclohexylamine	58 + 61 + 35
36	*O*,*O'*-Dimethylxanthocillin dihydrate	36 + 13 + 73
37	Ethanol	—
38	Ethanolic potassium hydroxide	72 + 22 + 38
39	Ethylene	39 + 40
40	Hydrogen cyanide	39 + 40
		32 + 40
		42 + 37 + 40 + Δ
41	Hydrogen hexacyanocobaltate	41 + 37 + 40 + Δ
42	Hydrogen hexacyanoferrate	42 + 37 + 40 + Δ
43	Hydroxyalkylformamides	43 + 61 + 82
44	Hydroxyarylformamides	44 + 61 + 82
45	*syn*-(Hydroxy)benzoinmonoxime	45 + 13 + 12
46	Hypobromite	11 + 46
47	Hypochlorite	47 + 81
48	Indole	48 + 60
49	Iodide	51 + 49
50	Isocyanates	50 + 88
51	Isocyanide dichlorides	87 + 51
		51 + 57
		51 + 49
52	Isocyanide metal complexes	52 + 71
53	Isothiocyanates	87 + 53
		67 + 53
		53 + 24
		53 + 90

TABLE I *continued*

Reagent		Reagent combination producing isocyanide (Δ = heat)
No.	Name	
54	*a*-Ketocarboxylic imide chlorides	54 + 12
55	*N*-Methyleneaniline	60 + 55
56	Methylketene diethylacetal	2 + 56 + 15
57	Methyl lithium	51 + 57
58	*N*-Monosubstituted formamides	58 + 73 + 13; 58 + 61 + 16 70 + 28 + 58; 58 + 61 + 34 58 + 61 + 82; 58 + 61 + 35 58 + 85 + 12; 58 + 61 + 89 58 + 62 + 73; 58 + 63 + 73 58 + 64 + 73; 58 + 65 + 73 58 + 66 + 73;
59	*N*-Monosubstituted thioformamides	59 + 27 + 12
60	Nitrosobenzene	60 + 48 60 + 55
61	Phosgene	58 + 61 + 82; 58 + 61 + 16 44 + 61 + 82; 43 + 61 + 82
62	Phosphorus oxychloride	58 + 62 + 73
63	Phosphorus pentachloride	63 + 58 + 73
64	Phosphorus pentoxide	64 + 58 + 73
65	Phosphorus tribromide	65 + 58 + 73
66	Phosphorus trichloride	66 + 58 + 73
67	Photolysis	67 + 53
68	2-Picoline	68 + 33
69	Potassium t-butoxide	17 + 69 + Δ 72 + 22 + 69 29 + 69
70	Potassium carbonate	—
71	Potassium cyanide	52 + 71
72	Primary amines	72 + 22 + 38 20 + 72 + 24 72 + 22 + 69 72 + 33
73	Pyridine	83 + 73 + 58
74	Quinazoline-3-oxide	74 + 1
75	Quinoline	75 + 58 + 13; 58 + 83 + 75 58 + 61 + 83; 75 + 61 + 58
76	Silver cyanide	8 + 76
77	Silver hexacyanocobaltates	Δ + alkylation product of 77 5 + alkylation product of 77
78	Silver hexacyanoferrates	Δ + alkylation product of 78 5 + alkylation product of 78
79	Sodium carbonate	23 + 79
80	Sodium trichloroacetate	80 + 10 + Δ 80 + 9 + Δ 80 + 84 + Δ
81	1-Substituted thiosemicarbazides	21 + 81 21 + 47

TABLE I *continued*

Reagent		Reagent combination producing isocyanide (Δ = heat)
No.	Name	
82	Tertiary amines	—
83	Toluenesulphonyl chloride	83 + 73 + 58; 19 + 12 + 83 2 + 12 + 83
84	*p*-Toluidine	84 + 80 + Δ
85	Thionyl chloride	58 + 85 + 12
86	Triethylamine	58 + 61 + 86
87	Triethylphosphine	51 + 87; 53 + 87
88	Triethyl phosphite	50 + 88
89	Trimethylamine	58 + 61 + 89
90	Triphenyltin hydride	53 + 88

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Summary—Information is provided on the design of olfactory detection reactions based on isocyanide formation. Potential detection, warning or identification schemes can be designed by scanning a listing of reagents or classes of compounds to be detected and then tabulating the reagent combinations which will produce isocyanides.

Zusammenfassung—Es werden Gesichtspunkte zur Ausarbeitung von Geruchsnachweisen mitgeteilt, die auf der Bildung von Isocyaniden beruhen. Schemata zu möglichen Nachweis-, Warn- oder Identifizierungsreaktionen können erstellt werden, indem man eine Liste von Reagentien oder nachzuweisenden Verbindungsklassen durchgeht und dann die Kombinationen von Reagentien tabelliert, die Isocyanide bilden können.

Résumé—On fournit des données sur l'étude de réactions de détection olfactive basées sur la formation de carbylamine. On peut dessiner des schémas possibles de détection, avertissement ou identification en examinant de manière approfondie une énumération de réactifs ou de classes de composés à détecter puis en répertoriant les combinaisons de réactifs qui vont produire des carbylamines.

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NOTICES

TENTH NATIONAL MEETING
SOCIETY FOR APPLIED SPECTROSCOPY

The Tenth National Meeting of the Society for Applied Spectroscopy will be held at Stouffer's Riverfront Inn in St. Louis, Missouri on 18–22 October 1971. Special symposia and general sessions on all areas of spectroscopy will be presented. For additional information please write to the General Chairman:

Miss Joan E. Westermeyer
Titanium Pigment Division
National Lead Company
Carondelet Station
St. Louis, Missouri 63111

FIFTH INTERNATIONAL VACUUM CONGRESS
and
1971 INTERNATIONAL CONFERENCE ON SOLID SURFACES

These meetings will be held on 11–15 October 1971 at the Sheraton-Boston Hotel, Boston, Mass., U.S.A. Abstracts of papers offered must reach the programme chairman by 19 May. The programme chairman is Dr. J. H. Singleton, Westinghouse R & D Center, Beulah Road, Pittsburgh, Pennsylvania 15235, and general information can be obtained from Dr. T. E. Madey, Secretary International Conference on Solid Surfaces, Surface Chemistry Section, Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, U.S.A.

Talanta, 1971, Vol. 18, pp. iii to iv. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

AAS-Bestimmung von Rhenium in den hochschmelzenden Metallen Wolfram, Molybdän und Tantal: G. M. NEUMANN. (21 *December* 1970)

Determination of aluminium in molybdenum and tungsten metals, iron, steel and ferrous and non-ferrous alloys with Pyrocatechol Violet: ELSIE M. DONALDSON. (21 *December* 1970)

Electrophoretic determination of pK values of indicators and their relation to colour changes: I. MORI, E. FALK, M. SHINOGI and Y. KISO. (28 *December* 1970)

Identification and estimation of LSD and other lysergic acid derivatives by luminescence spectroscopy: A. BOWD, J. B. HUDSON and J. H. TURNBULL. (28 *December* 1970)

Dehydroacetic acid as a reagent for the separation and gravimetric determination of copper(II), aluminium and beryllium: GURCHARAN SINGH MANKU and PRABHU DAYAL SARPAL. 28 *December* (1970)

Electrochemical studies of indium with some monocarboxylic acids at the dropping mercury electrode: O. N. SHRIVASTAVA, J. K. GUPTA and C. M. GUPTA. (28 *December* 1970)

Spectrophotometric determination of ruthenium with diphenylthiovioluric acid: R. S. CHAWLA, R. P. SINGH and K. C. TRIKHA. (29 *December* 1970)

Spectrophotometric determination of critical micelle concentration of non-ionic surfactants: PURAN CHAND and V. P. AGARWALA. (29 *December* 1970)

New methods for the use of acriflavine in the detection of the carboxylic acid group in organic compounds: G. S. JOHAR and H. S. SODHI. (30 *December* 1970)

Use of 2,3,4-trihydroxyacetophenone in inorganic analytical chemistry: N. V. DESHPANDE, B. G. KAMBLE and A. J. MUKHEDKAR. (7 *January* 1971)

Cation-exchange separation of uranium from other elements in tetrahydrofuran–nitric acid media containing trioctylphosphine oxide: M. M. KHATER and J. KORKISCH. (7 *January* 1971)

Spectroscopy in separated flames—VII. The determination of bismuth by atomic-fluorescence spectroscopy in a separated air–acetylene flame, using electronically modulated electrodeless discharge tube sources: R. S. HOBBS, G. F. KIRKBRIGHT and T. S. WEST. (8 *January* 1971)

Determination of 0.01–0.1% of samarium in 40–100 mg of lead chloride: J. AGTERDENBOS, B. A. H. G. JUTTE and J. SCHURING. (8 *January* 1971)

Determination of phosphorus in coke by the oxygen-flask method: B. P. KIRK and H. C. WILKINSON. (12 *January* 1971)

Spectrophotometric study of iron(III) complexes of 7-nitro-8-quinolinol-5-sulphonic acid: S. K. PATEL, K. P. SONI and I. M. BHATT. (14 *January* 1971)

Spectrochemical determination of the rare earths in uranium and its salts: B. ZMBOVA, M. TRIPKOVIĆ and O. ŠEĆEROV. (14 *January* 1971)

Detection of *cis* and *trans* isomers by NMR: N. S. BIRADAR and M. A. PUJAR. (15 *January* 1971)

AAS-Bestimmung von Natrium und Kalium in den hochschmelzenden Metallen Wolfram und Molybdän: G. M. NEUMANN. (15 *January* 1971)

Zur Verbesserung der Reproduzierbarkeit der Meßwerte bei photometrischen Bestimmungsverfahren: S. KOCH and G. ACKERMANN. (9 *February* 1971)

Rapid dissolution of sulphide ore for the determination of copper: W. C. HOYLE and H. DIEHL. (9 *February* 1971)

Electrochemical behaviour of aluminium(III) and beryllium(II) perchlorates in dimethylformamide: M. GALOVA and D. A. PANTONY. (16 *February* 1971)

Arsenic and selenium determination in steel by an X-ray and prechemical concentration technique: G. L. VASSILAROS. (22 *February* 1971)

Microdosage du carbone dans les composés organiques par combustion quasi-instantanée et titrage coulometrique automatique du dioxyde de carbone: D. FRAISSE. (25 *February* 1971)

Indirect near-infrared spectrophotometric determination of silicon by the 2-amino-4-chlorobenzenethiol method: LOUIS A. TRUDELL and D. F. BOLTZ. (1 *March* 1971)

The practical analysis of high purity chemicals—IV. Precision silver chloride gravimetry: K. LITTLE. (9 *March* 1971)

Interferences and their elimination in the determination of the noble metals by atomic-absorption spectrophotometry: R. C. MALLETT, D. C. G. PEARTON, E. J. RING and T. W. STEELE. (10 *March* 1971)

Microtitrimetric determination of uranium in nitric acid medium in the presence of excess of iron, magnesium and aluminium: V. MAREŠKA. (15 *March* 1971)

Masking agents in metal titration with EDTA—V. Titration of rare-earth elements in the presence of some other metals: A. C. SPÍNOLA COSTA and T. M. TAVARES. (15 *March* 1971)

Determination of inorganic impurities in monovinyl chloride by activation analysis: FLORIN T. BUNUS and SANDA MURGULESCU. (15 *March* 1971)

An improved colorimetric determination of vanadium in geochemical prospecting samples: J. L. ROBERTS. (15 *March* 1971)

Rapid solvent extraction and direct spectrophotometric determination of lead(II) with thiothenoyltrifluoroacetone: S. B. AKKI and S. M. KHOPKAR. (16 *March* 1971)

Ammonium hexanitratocerate(IV) as an oxidizing agent—V. Titrimetric determination of arsenic(III) at room temperature with visual and potentiometric end-points: G. GOPALA RAO, K. S. MURTY and MURALIKRISHNA GANDIKOTA. (16 *March* 1971)

Ammonium hexanitratocerate(IV) as an oxidizing agent—VI. Determination of chromium(III) through oxidation to chromium(VI) at room temperature: G. GOPALA RAO, K. S. MURTY and MURALIKRISHNA GANDIKOTA. (16 *March* 1971)

Organic analysis by luminescence methods: J. BARTOS and M. PESEZ. (17 *March* 1971)

Catalytic method for the determination of cobalt impurities in reactor cooling-water circuits: G. E. BATLEY. (17 *March* 1971)

Talanta, 1971, Vol. 18, p. v. Pergamon Press. Printed in Northern Ieland

PUBLICATIONS RECEIVED

Four-Language Technical Dictionary of Chromatography (English/German/French/Russian): Ed. H.-P. ANGELÉ. Pergamon Press, Oxford, 1970. Pp. 119. £5.

Chromatographic literature in English is spattered with terms of such limited currency that the similar situation prevailing in literature in other languages often involves guessing which of many translations is the correct one; the frequency of synonyms and the use of laboratory jargon makes this task hazardous. The Four-Language Dictionary of Chromatography (English/French/German/Russian) will reduce the dangers of mistranslation. The dictionary wisely includes many synonyms in each language although some of the names for compounds are rarely used. The dictionary could more aptly be named a Dictionary of Fractionation Methods as some of the methods are not chromatographic. The coverage is good and in general the "missing" words can be found in a less specialized dual-language chemical dictionary. There is no mention, however, of porous-glass chromatography. The mode of compilation makes this primarily a dictionary for locating the English translation of French, German or Russian words or phrases but with very little difficulty it can be used for translation from any of these languages into one of the others.

The Chemical Analysis of Foods, 6th Ed.: DAVID PEARSON. Churchill, London, 1970. Pp. xii + 604. £6.

This valuable book is not only a mine of information on methods of food analysis but also on the composition of foods and on the legal requirements for purity *etc.* It provides the general reader with much interesting material, and the specialist with a reliable laboratory guide.

Progress in Separation and Purification, Vol. 3: ed. EDMOND S. PERRY and CAREL J. VAN OSS. Wiley, New York, 1970. Pp. xi + 316. $19.95.

With chapters on Vapor-Programmed Thin-Layer Chromatography, "Dry-Column" Chromatography, Ultrafiltration Membranes, High-Pressure Gas Chromatography, Plasticizing Effect of Permeates on Membrane Permeation and Separation, Separation and Purification by Reverse Osmosis, Progress in Inorganic Thin-Layer Chromatography, and Separation of Nickel and Cobalt by an Electrolytic Process, this volume continues to follow the trend and standards set by its predecessors in the series.

Spectral Data of Natural Products, Vol. 1: K. YAMAGUCHI. Elsevier, Amsterdam, 1971. Pp. v + 765. $60.

This first part of a massive compilation of data gives information on the NMR, UV and IR spectra of some 2300 compounds. The work is likely to prove a useful literature guide for the worker in the field of natural products.

SUMMARIES FOR CARD INDEXES

Coulometric microdetermination of water: RONALD KARLSSON and K. J. KARRMAN, *Talanta*, 1971, **18**, 459. (Department of Analytical Chemistry, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden.)

Summary—An electroanalytical method for the determination of small amounts of water by controlled potential coulometry has been devised. Excess of iodine is produced coulometrically in a Karl Fischer reagent, the sample is added, and after complete reaction the remainder of the iodine is reduced. The number of coulombs consumed in the cell reaction is determined by integration of the current by means of an electronic integrator. Karl Fischer reagents of various compositions were checked to find the most satisfactory conditions and a special electrolysis cell for water determination was constructed entirely in glass and Teflon. Samples containing 0·1–2 mg of water were added and determined with an accuracy of ±0·15%. The analysis times were 3–12 min.

The error in absorption measurements, caused by the use of non-monochromatic light—I. Parabolic functions: J. AGTERDENBOS and J. VINK, *Talanta*, 1971, **18**, 467. (Laboratory for Analytical Chemistry, State University, Croesestraat 77a, Utrecht, The Netherlands.)

Summary—The errors in absorption measurements in spectrophotometry, caused by the use of non-chromatic light, have been calculated. Parabolic functions have been assumed for the wavelength-dependence of the intensity of the incident light falling on the cell and of the absorbance of the compound measured. Results of the calculations may be used to predict non-linearity of absorbance-concentration curves or photometric titration curves.

Determination of silver in ores and metallurgical concentrates by a combination of fire-assay preconcentration (using tin as collector) and atomic-absorption spectrophotometry: P. E. MOLOUGHNEY and J. A. GRAHAM, *Talanta*, 1971, **18**, 475. (Fire-Assay Laboratory, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.)

Summary—A new method is described for the determination of silver in ores and metallurgical concentrates. The procedure is based on collection of silver in a tin button during a fire assay fusion, and the subsequent determination by atomic-absorption spectrophotometry. The proposed method is rapid, free from interelement interferences, and results obtained agree favourably with those obtained by alternative methods.

МИКРООПРЕДЕЛЕНИЕ ВОДЫ КУЛОНОМЕТРИЧЕСКИМ МЕТОДОМ:

RONALD KARLSSON and K. J. KARRMAN, *Talanta*, 1971, **18**, 459.

Резюме—Разработан электроаналитический метод определения небольших количеств воды методом кулонометрии с контроллированным напряжением. Производят кулонометрическим путем избыток иода в Карла Фишера реагенте, добавляют пробу и после окончанной реакции восстанавливают оставшийся иод. Число кулонов потребленных в реакции в ячейке определяют интегрированием тока с использованием электронного интегратора. Изучены различные состави Карла Фишера реагента с целью установить самые лучшие условия и сконструирована только из стекла и тефлона специальная электролитическая ячейка для определения воды. Добавлены пробы содержащие 0,1–2 мг воды и определены точностью ±0,15 %. Продолжительность анализа 3–12 мин.

ОШИБКА ПРИ ИЗМЕРЕНИИ СВЕТОПОГЛОЩЕНИЯ ВЫЗВАННАЯ ПРИМЕНЕНИЕМ НЕМОНОХРОМАТИЧЕСКОГО СВЕТА—I. ПАРАБОЛИЧЕСКИЕ ФУНКЦИИ:

J. AGTERDENBOS and J. VINK, *Talanta*, 1971, **18**, 467.

Резюме—Вычислены ошибки при измерении светопоглощения вызванные применением немонохроматического света. Предпоставлены параболические функции для зависимости длины волн от интенсивности света падающего на кюветку и от светопоглощения измеримого соединения. Вычисленными результататми можно пользоваться для предсказания нелинейности кривых светопоглощения в зависимости от концентраии или кривых фотометрического титрования.

ОПРЕДЕЛЕНИЕ СЕРЕБРА В РУДАХ И МЕТАЛЛУРГИЧЕСКИХ КОНЦЕНТРАТАХ КОНЦЕНТРАЦИЕЙ СУХИМ ПУТЕМ (ПОЛЬЗУЯСЬ ОЛОВОМ В КАЧЕСТВЕ КОЛЛЕКТОРА) С ПОСЛЕДУЮЩИМ ОПРЕДЕЛЕНИЕМ МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОМЕТРИИ:

P. E. MOLOUGHNEY and J. A. GRAHAM, *Talanta*, 1971, **18**, 475.

Резюме—Описан новый метод определения серебра в рудах и металлургических концентратах. Метод основан на накоплении серебра в королке олова полученном плавлением и последующем определении методом атомно-абсорбционной спектрометрии. Предложенный метод является быстрым, свободным от интерэлементарных мешаний, а полученные результаты хорошо соглашаются с результатами полученными другими методами.

U(VI) complexes of oxine and derivatives: A. Corsini, J. Abraham and M. Thompson, *Talanta*, 1971, **18**, 481. (McMaster University, Hamilton, Ontario, Canada.)

Summary—Infrared bands due to the hydrogen-bonded $^+N—H \cdots O$ system in the oxine adduct of U(VI) have been identified and found to occur in the spectra of several newly prepared U(VI) adducts of oxine derivatives. Interligand steric effects in the U(VI) complexes of most 7-substituted oxines prevent the formation of the 1:3 adduct. Complexes of the type ML_2X, where X is a small co-ordinating species present in solution, are formed instead. With 2-substituted oxines, steric interactions between the 2-substituent and co-ordinated water result in destabilization of the complex and subsequent hydrolysis as the pH of the solution is raised. Experiments involving the use of [^{14}C]-oxine were found to distinguish between co-ordinated and lattice-held oxine and are potentially valuable in studies of oxine adducts formed by other metal ions.

Spectrophotometric determination of cyanide with organic disulphides: Ray E. Humphrey and Willie Hinze, *Talanta*, 1971, **18**, 491. (Department of Chemistry, Sam Houston State University, Huntsville, Texas 77340, U.S.A.)

Summary—The reaction of cyanide ion with the disulphides 2,2′-dithiodipyridine, 4,4′-dithiodipyridine, 2,2′-dithiodipyrimidine and 5,5′-dithiobis(2-nitrobenzoic acid) to displace an absorbing thiol anion has been evaluated for the spectrophotometric determination of cyanide. Reaction is somewhat slow and is applicable to cyanide determination in the range 0·2–5·0 μg/ml. By variation of reactant ratios and pH the concentration range can be increased to 50 μg/ml. The reaction is faster when cyanide is present at a higher concentration than the disulphide.

Infrared determination of barium, strontium, sodium and potassium sulphates by the pellet technique: David E. Chasan and George Norwitz, *Talanta*, 1971, **18**, 499. (Frankford Arsenal, Philadelphia, Pa. 19137, U.S.A.)

Summary—Methods are proposed for the infrared determination of barium, strontium, sodium and potassium sulphates by the pellet technique. The semimicro sample is mixed with 300 mg of potassium bromide, the pellet is formed, and the peak heights are determined at the appropriate peak. Barium and strontium sulphates are measured at 983 and 993 cm^{-1}, respectively. Sodium and potassium sulphates are both measured at 619 cm^{-1}. Barium and strontium sulphates can be determined in the presence of each other in ratios from 1:20 to 20:1 from the measurements at 983 and 993 cm^{-1}. Carbonates or nitrates do not interfere with any of the procedures.

КОМПЛЕКСЫ U(VI) С ОКСИНОМ И ЕГО ПРОИЗВОДНЫМИ:

A. Corsini, J. Abraham and M. Thompson, *Talanta*, 1971, **18**, 481.

Резюме—Идентифицированы полосы в инфракрасном спектре вызванные содержащей водородную связь системой $^+N—H \cdots O$ в комплексе оксина с U(VI). Эти полосы обнаружены в спектрах ряда новоприготовленных комплексов U(VI) с дериватами оксина. Межлигандовые пространственные эффекты в комплексах U(VI) с большинством 7-замещенных оксинов препятствуют образованию 1:3 комплекса. Вместо этого образуются комплексы типа ML^2X, где X представляет собой небольший координирующий род присутствующий в растворе. В случае 2-замещенных оксинов, в результате пространственных взаимодействий между 2-заместителем и координированной водой появляется дестабилизация комплекса с последующим гидролизом вследствие повышения pH раствора. Опыты с использованием (^{14}C)-оксина позволили различать между координированным и удержанным в решётка оксином; они представляют несомненный интерес для изучения комплексов оксина с другими ионами металлов.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЦИАНИДА С ИСПОЛЬЗОВАНИЕМ ОРГАНИЧЕСКИХ ДИСУЛЬФИДОВ:

Ray E. Humphrey and Willie Hinze, *Talanta*, 1971, **18**, 491.

Резюме—Изучена реакция цианидиона с дисульфидами 2,2′-дитиопиридин, 4,4′-дитиопиридин, 2,2′-дитиопиримидин и 5,5′-дитиобис(2-нитробензойная кислота), для вытеснения поглощающего тиолового аниона с целью применения в спектрофотометрическом определении цианида. Реакция несколько медленная, она применима в определении цианида в пределах 0,2–5,0 мкг/мл. Изменением отношения реактантов и pH раствора можно протянуть пределы концентраций до 50 мкг/мл. Реакция быстрее если цианид присутствует в концентрациях больших концентрации дисульфида.

ОПРЕДЕЛЕНИЕ СУЛЬФАТОВ БАРИЯ, СТРОНЦИЯ, НАТРИЯ И КАЛИЯ МЕТОДОМ ИНФРАКРАСНОЙ СПЕКТРОСКОПИИ С ИСПОЛЬЗОВАНИЕМ ЛИСКА БРОМИДА КАЛИЯ:

David E. Chasan and George Norwitz, *Talanta*, 1971, **18**, 499.

Резюме—Предложены методы определения сульфатов бария, стронция, натрия и калия методом инфракрасной спектроскопии с использованием диска бромида калия. Полумикропробу смешивают с 300 мг бромида калия, образуют диск и измеряют высоту соответственных пиков. Сульфаты бария и стронция измеряют при 983 и 993 $см^{-1}$, соответственно, а натрия и калия—при 619 $см^{-1}$. Сульфаты бария и стронция можно определять одного в присутствии другого в отношениях 1:20 до 20:1, на основе измерений при 983 и 993 $см^{-1}$. Карбонаты и нитраты не мешают этим определениям.

Coulometric determination of Ce(III) in alkaline solutions with electrogenerated octacyanomolybdate(V): R. Córdova-Orellana and F. Lucena-Conde, *Talanta*, 1970, **18**, 505. (Department of Analytical Chemistry, Faculty of Sciences, Salamanca, Spain.)

Summary—The coulometric determination of Ce(III) with octacyanomolybdate(V) in concentrated carbonate–bicarbonate buffer solutions was carried out. The current efficiency for electrogeneration of octacyanomolybdate(V) and the optimum conditions for analytical determinations of microquantities of cerium have been investigated.

Film stripping voltammetry: Kh. Z. Brainina, *Talanta*, 1971, **18**, 513. (Department of Physical and Analytical Chemistry, Sverdlovsk Institute of National Economy, Sverdlovsk 26, ul. Dekabristov 20, U.S.S.R.)

Summary—Film stripping voltammetry is a new electrochemical analytical method consisting in concentrating the test substance in the form of a metal or a sparingly soluble compound on the electrode surface and subsequently recording the current for electrodissolution of the deposit. The method has been worked out for determination of metal ions, anions and variable valence ions, with sensitivities as low as $10^{-9}M$. As indicator electrodes, solid, usually graphite, electrodes and stationary mercury electrodes are used.

Anion-exchange separations of metal ions in thiocyanate media: James S. Fritz and Edward E. Kaminski, *Talanta*, 1971, **18**, 541. (Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.)

Summary—The analytical potential of weak-base macroreticular anion-exchange resin for the quantitative separation of metal ions in thiocyanate media is investigated and demonstrated. Distribution data are given for the sorption of some 25 metal ions from aqueous mixtures of potassium thiocyanate ($1.0M$ or less) and $0.5M$ hydrochloric acid. The magnitude of the distribution data suggests many possible separations, some of which were quantitatively performed by procedures which are fast, simple and require only mild conditions. Representative separations are removal of traces of iron(III) and copper(II) from water samples prior to the determination of water hardness (calcium and magnesium), separation of nickel(II) from vanadium(IV) and the separation of thorium(IV) from titanium(IV). Some multicomponent separations are the separation of rare earths(III) and thorium(IV) from scandium(III) and the separation of rare earths(III) from iron(III) and uranium(VI).

КУЛОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ Ce(III) ЭЛЕКТРОГЕНЕРИРОВАННЫМ ОКТАЦИАНОМОЛИБДАТОМ(V) В ЩЕЛОЧНЫХ РАСТВОРАХ:

R. Córdova-Orellana and F. Lucena-Conde, *Talanta*, 1971, **18**, 505.

Резюме—Проведено кулонометрическое определение Ce(III) октацианомолибдатом(V) в концентрированных буферных растворах карбоната-бикарбоната. Исследованы эффективность тока и оптимальные условия для аналитического определения микроколичеств цера.

ВОЛЬТАМПЕРОМЕТРИЯ С СНИМАНИЕМ ПЛЁНКИ:

Kh. Z. Brainina, *Talanta*, 1971, **18**, 513.

Резюме—Вольтамперометрия с сниманием плёнки представляет собой новый метод электрохимического анализа, основывающийся на концентрировании испытуемого вещества в форме металла или почти нерастворимого вещества на поверхности электрода, с последующим записыванием тока потребного для электрорастворения осадка. Метод разработан для определения ионов металлов, анионов и ионов переменной валентностью с чувствительностью до $10^{-9}M$. Твёрдые электроды—обычно графитовые—и стационарные ртутные электроды использованы в качестве индикаторных электродов.

РАЗДЕЛЕНИЕ ИОНОВ МЕТАЛЛОВ В РОДАНИДНЫХ СРЕДАХ С ИСПОЛЬЗОВАНИЕМ АНИОНООБМЕННИКОВ:

James S. Fritz and Edward E. Kaminski, *Talanta*, 1971, **18**, 541.

Резюме—Исследована и показана применимость в анализе слабо основных макроретикулярных анионообменных смол в количественном разделении ионов металлов в роданидных средах. Приведены данные для распрéделения при сорбции 25 ионов металлов из водных растворов роданида калия (1,0*M* или меньше) и 0,5*M* соляной кислоты. Данные для распределения указывают на проведимость ряда разделений; некоторые из них дали количественные разделения с применением быстрых и несложных методов, погребующих только мягкие условия. Характеристичные разделения представляют собой устранение следов железа(III) и меди(II) из образцов воды перед определением жёсткости воды (кальция и мавния), отделение никеля(II) от ванадия(IV) и отделение тория(IV) от титана(IV). В качестве примера для многокомпонентных разделений приведены от Деление редкоземельных элементов(III) и тория(IV) от скандия(III) и отделение редкоземельных элементов (III) от железа (III) и урана (VI).

Chelatbildende Austauscherharze—XI. Abtrennung des Be(II) vom Al(III) am Chelataustauscher auf der Basis von *o*-(2-Hydroxyphenylazo) benzoesäure: E. Blasius, K.-P. Janzen and W. Fallot-Burghardt, *Talanta*, 1971, **18**, 549. (Institut für Analytische Chemie und Radiochemie der Universität des Saarlandes, 6600 Saarbrücken, B.R.D.)

Summary—A chelate-exchanger based on *o*-(2-hydroxyphenylazo)-benzoic acid is used for the rapid and quantitative separation of beryllium from aluminium. Aluminium is eluted with $4M$ ammonium acetate, and beryllium with $2M$ hydrochloric acid.

Design of olfactory detection reactions based on isocyanide formation: E. J. Poziomek, *Talanta*, 1971, **18**, 553. (Defensive Research Department, Physical Research Laboratory, Edgewood Arsenal, Maryland 21010, U.S.A.)

Summary—Information is provided on the design of olfactory detection reactions based on isocyanide formation. Potential detection, warning or identification schemes can be designed by scanning a listing of reagents or classes of compounds to be detected and then tabulating the reagent combinations which will produce isocyanides.

ХЕЛАТООБРАЗУЮЩИЕ ИОНООБМЕННЫЕ СМОЛЫ—XI. ОТДЕЛЕНИЕ Be(II) ОТ Al(III) НА ХЕЛАТООБМЕННИКЕ НА ОСНОВЕ о-(2-ОКСИФЕНИЛАЗО)-БЕНЗОЙНОЙ КИСЛОТЫ:

E. Blasius, K.-P. Janzen and W. Fallot-Burghardt, *Talanta*, 1971, **18**, 549.

Резюме—Основывающийся на о-(2-оксифенилазо) бензойной кислоте хелатообменник использован для быстрого и количественного отделения бериллия от алюминия. Бериллий элюируют $4M$ ацетатом аммония, а алюминий—$2M$ соляной кислотой.

РАЗРАБОТКА РЕАКЦИЙ ОБОНЯТЕЛЬНОГО ОБНАРУЖЕНИЯ ОСНОВЫВАЮЩИХСЯ НА ОБРАЗОВАНИИ ИЗОЦИАНИДА:

E. J. Poziomek, *Talanta*, 1971, **18**, 553.

Резюме—Описана разработка реакций обонятельного обнаружения основывающихся на образовании изоцианида. Можно создать системы обнаружения предупреждения или идентификации рассмотрением списка реагентов или обнаруживаемых родов соединений, с последующим табеллированием комбинаций реагентов которые дают изоцианиды.

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