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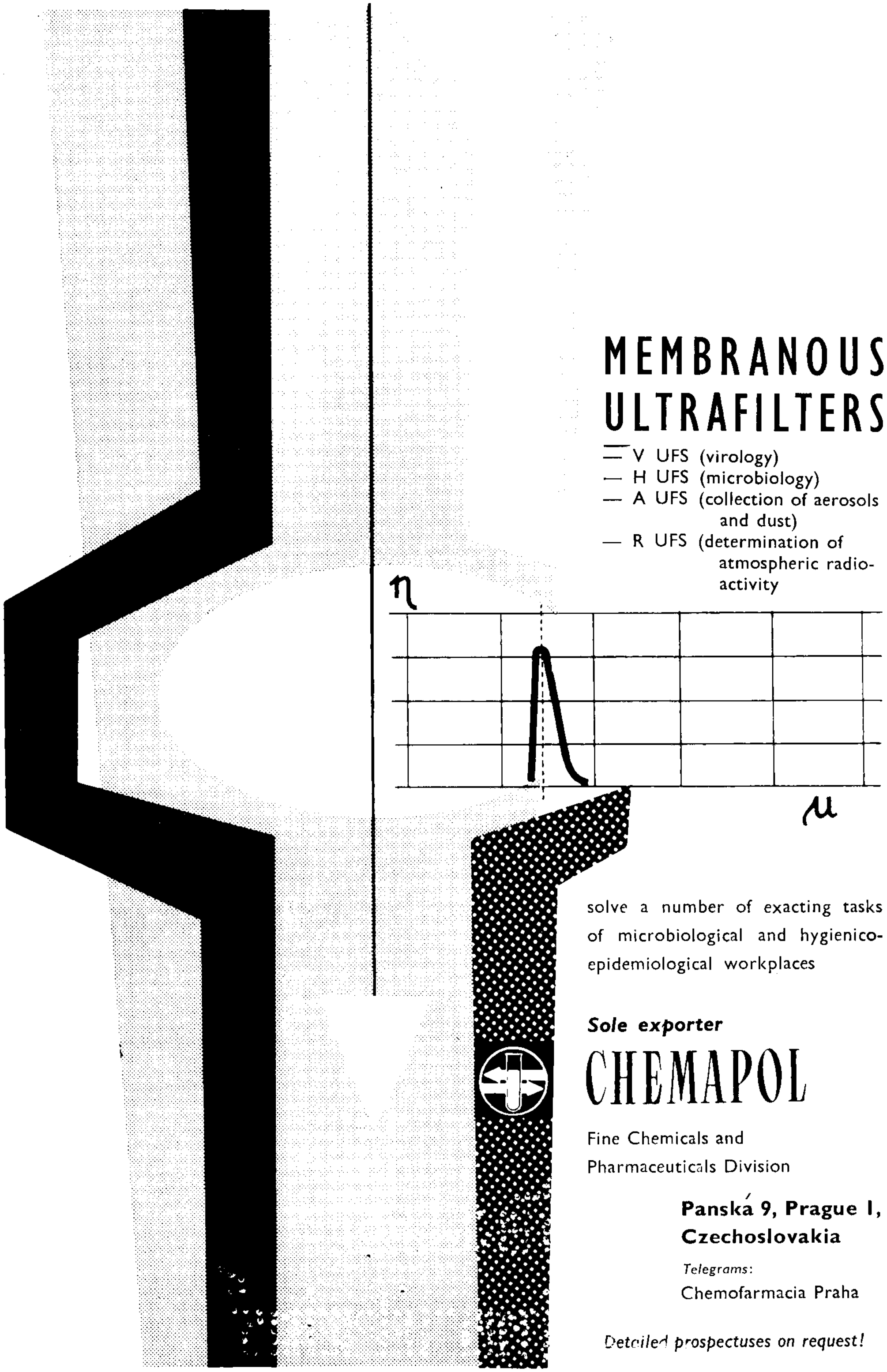
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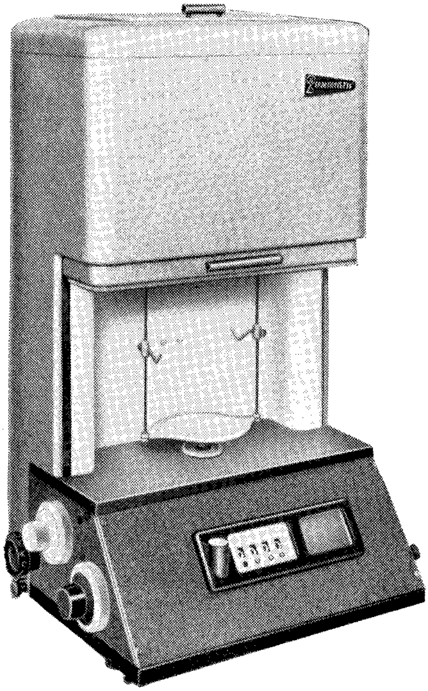

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SUMMARIES FOR CARD INDEXES

A polarographic study of dissolved oxygen—II: V S GRIFFITHS and M. I. JACKMAN, *Talanta*, 1962, **9**, 871.

Summary—An investigation of the two oxygen reduction waves in aqueous potassium chloride has been made. The first wave is reversible to a considerable degree, the second almost irreversible.

The determination of traces of arsenic and antimony in samples of platinum by neutron-activation analysis: R. A. KILLICK and D. F. C. MORRIS, *Talanta*, 1962, **9**. 879.

Summary—A method is described for the determination of ultramicro quantities of arsenic and antimony in pure platinum. In order to avoid self-shielding differences between samples and standards during neutron irradiation, comparators have been prepared by the addition of very small known amounts of arsenic and antimony to analytical samples. The nuclear reactor BEPO at Harwell has been used as the neutron source; 0·1-g samples of platinum have been taken for the determinations, and a radiochemical separation procedure using carriers has been employed to isolate the induced arsenic and antimony activities.

Results of analyses of seven samples of platinum are quoted. Although contents of as little as 10^{-8} g of either arsenic or antimony were determined, the ultimate sensitivity of the method was not approached.

The ultraviolet spectra of chlorine and its oxides: ZDENEK SPURNÝ, *Talanta*, 1962, **9**, p. 885.

Summary—Chlorine and its oxides (Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7) give ultraviolet absorption spectra in carbon tetrachloride. These spectra can be used for the determination of the compounds.

The influence of the nature of the organic solvent on the extraction of chelate compounds: I. P. ALIMARIN and YU. A. ZOLOTOV *Talanta*, 1962 **9**, 891.

Summary—The influence of the nature of the organic solvent on the extraction of the thenoyltrifluoroacetonates of Np^{V}, Co^{II} and Ce^{III}, the hydroxyquinolates of Np^{V} and W^{VI}, the acetylacetonates of Co^{II} and Fe^{III}, the 1-nitroso-2-naphtholate of Co^{II}, and some other chelate compounds has been studied. As a rule, "co-ordination-unsaturated" chelates (co-ordination number of the central atom greater than twice its charge, bidentate reagent) are extracted better by ketones, esters, and, particularly, by alcohols; and, normally, are less well extracted by ethers and by hydrocarbons and their halogen-substituted derivatives. The extraction of "co-ordination-unsaturated" chelates can in some cases be favoured by the use of an excess of the reagent. "Co-ordination-saturated" chelate compounds (co-ordination number not greater than twice the charge, bidentate reagent) can be extracted by solvents of extremely diverse nature, including non-oxygen-containing solvents of relatively low polarity. Attention is drawn to the possibility of separating "co-ordination-saturated" and "co-ordination-unsaturated" chelate compounds.

An I–Q Recorder and its application to rapid coulometric analysis and micro-coulometry: S. Hanamura, *Talanta*, **9**, 901, 1962.

Summary—The author recently described a direct-reading current integrator and subsequently improved it into a recording instrument, the I–Q recorder. It can be used not only for coulometric analysis but also for other purposes. The highest sensitivity range is 10 μA; the reproducibility can be assumed to be 0·1%. Integration is possible from input zero to rated value. Rapid determination of micro amounts of copper and lead, 1–10 μg and 4–10 μg respectively, has been carried out. Rapid determination of 0·9 mg of lead and 0·8 mg of cadmium from their mixtures is discussed.

Exchange equilibria involving complexans—II: General consideration and scope applications in analytical chemistry: Genkichi Nakagawa and Motoharu Tanaka, *Talanta*, 1962, **9**, 917.

Summary—For several cases of practical importance in analytical chemistry, the following exchange equilibrium has been considered theoretically:

$$\mathrm{NY} + \mathrm{M} + n\mathrm{A} \rightleftharpoons \mathrm{MY} + \mathrm{NA}_p$$

In favourable conditions, the determination of a metal M can be substituted by that of a second metal N using various methods including polarography, photometry, solvent extraction, *etc.* Factors influencing such an indirect determination are discussed in detail. Extending the argument, an equation has been proposed to express the colour change in the vicinity of the equivalence point in the chelatometry of M using the NY-A system as indicator. It is possible to find the optimum condition for a given problem if the stability constants of the various species involved in the above exchange equilibrium are available.

The polarography of silver: R. M. Dagnall and T. S. West, *Talanta*, 1962, **9**, 925.

Summary—A true polarographic wave for silver may be obtained in a cyanide medium from which the excess of unreacted cyanide ion is removed by addition of excess of nickel ions. None of the common anions interferes, even thiosulphate, nor do any of the metals examined except Tl^+. The coincident wave of Pb^{2+} may be removed to more cathodic potentials by addition of excess of ethylenediaminetetra-acetic acid.

Detection and estimation of some polynuclear hydrocarbons by electron spin resonance: B. D. Flockhart and R. C. Pink, *Talanta*, 1962, **9**, 931.

Summary—Certain polynuclear hydrocarbons are quantitatively converted into the free radical form on the surface of a strongly dehydrated silica-alumina catalyst. The resulting radical species are stable in the adsorbed state and their detection and estimation by electron spin resonance technique is described. Less than 10^{-10} mole of hydrocarbon can be detected. The application of this technique to the estimation of anthracene, perylene, dimethylanthracene and naphthacene is described.

Triethylene tetramine-N,N,N′,N′,N;,N;-hexa-acetic acid as a new titrimetric reagent: Rudolf Přibil and Vladimír Veselý, *Talanta*, 1962, **9**, 939.

Summary—Disodium salt of triethylene tetramine hexaacetic acid (TTHA) has been used for complexometric determination of a great number of metals. The existence of bimetallic complexes of most bivalent elements has been proved. Tervalent elements form bimetallic complexes too, except bismuth, thalium, indium and lanthanum. By using EDTA and TTHA as volumetric reagents it is possible to determine some couple elements without screening reagents. The new type of displacement reactions:

$$Me_2X + 2Y = 2MeY + X$$
$$MeX + Y = MeY + X$$

(X and Y are the anions of TTHA and EDTA) can be used for complexometric determinations. These possibilities have been briefly discussed.

4-(2-Pyridylazo)resorcinol as a selective and sensitive spectrophotometric reagent for niobium^{V} V: R. Belcher, T. V. Ramakrishna and T. S. West, *Talanta*, 1962, **9**, p. 943.

Summary—The reagent 4-(2-pyridylazo) resorcinol, PAR, in the presence of EDTA, gives a colour reaction with quinquevalent niobium which is not interfered with by any of the metals which normally accompany niobium. Of some 30 cations examined, only uranium^{VI} and vanadium^{V} interfere seriously. The reaction provides a sensitive method for the spectrophotometric determination of niobium, and is also applicable as a spot test for amounts of niobium^{V} down to 0.1 μg. Even tantalum does not interfere when present in twenty-fold amounts, provided sufficient tartrate ion is added.

Pyrohydrolytic determination of fluoride in milligram quantities of plutonium fluorides; C. S. Rao and M. S. Subramangan: *Talanta*, **9**, 947.

Summary—The pyrohydrolytic determination of fluoride using moist air is described for the fluoride content of plutonium fluorides on the milligram scale.

Separation and determination of microgram or submicrogram quantities of gold in copper: Use of mercury as a collector: A Mizuike, *Talanta*, 1962, **9**, 948.

Summary—A new method of separation is described and applied to the determination of trace amounts of gold in copper metal. Gold is deposited into mercury globules from an ammoniacal solution of the copper The resulting amalgam is heated to remove mercury, and gold in the residue is determined by the photometric *p*-dimethylaminobenzylidenerhodanine method As little as 0 01 ppm of gold in copper can be separated and determined by the proposed method.

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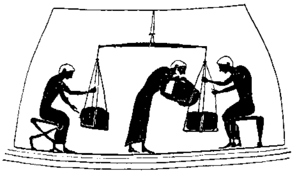
An International Journal of Analytical Chemistry



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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.

[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.

[4] W. Jones, *Brit. Pat.* 654321, 1959.

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A POLAROGRAPHIC STUDY OF DISSOLVED OXYGEN—PART II*

V. S. GRIFFITHS† and M. I. JACKMAN‡

Received 8 *January* 1962. *Accepted* 15 *February* 1962.

Summary—An investigation of the two oxygen reduction waves in aqueous potassium chloride has been made. The first wave is reversible to a considerable degree, the second almost irreversible.

ONE of the most interesting aspects of the study of dissolved oxygen is the degree of reversibility of its reduction at the dropping mercury electrode. Heyrovsky[1] has suggested that the reversibility of this electrode process may be hindered by the unlikelihood of direct capture, by an ion, of two electrons simultaneously; Glasstone[2] has pointed out that non-reversible reactions occur most frequently with non-ionised substances. It has, however, been stated by Breyer[3] that the reduction of oxygen is reversible in alkaline solution.

The second-stage reduction (of hydrogen peroxide) was studied by Chodkowski[4] at pH 13·5–14·2 and was found to be reversible.

A close study of the oxygen–peroxide couple was made by Kern,[5] who found that at pH values above 11 the couple is completely reversible.

Evidence for reversibility may also be obtained from the standard electrode potential of a substance; this has, in fact, been done by Berl[6] who has shown that the electrode reaction at activated carbon electrodes in strongly basic solutions is reversible, being equivalent to an oxygen electrode whose potential corresponds to the reaction:

$$O_2 + H_2O + 2e \rightleftarrows OH^- + HO_2^-.$$

This reaction is also put forward by Hickling[7] who deduces that the discharge of $OH^- \rightarrow OH + e$ is rapid. Kern,[5] however, considers that the HO_2^- ion itself is discharged and that the OH^- ion acts merely as a proton acceptor, while Heyrovsky[8] favours a direct reduction of the oxygen molecule.

In non-basic media Busch and Saywer,[9] Breyer,[3] and others state that both reductions are irreversible. Both Hacobian[10] and Kalousek,[11] however, have concluded that the first reduction of oxygen in unbuffered neutral solutions is reversible. This may be because AC polarographic techniques were employed in these studies, since it has been reported by Glasstone[12] that the oxygen overpotential is reduced by the superimposition of AC, this reduction in effect corresponding to an increase in reversibility. This agrees with the fact that Bowden and Keenan[13] found that in alkaline solutions the oxygen overpotential decreased as the hydroxyl ion concentration increased.

Von Stackelberg[14] and Kolthoff and Miller[15] state that both reductions are irreversible in all media, the latter having studied the reduction of oxygen in various buffers at pH values between 1 and 10.

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* Part I—*Talanta*, 1962, **9**, 205.

† Battersea College of Technology, London. S.W.11, England.

‡ Gas Council, London Research Station, Fulham, London, S.W.6, England.

The observation by Kolthoff and Miller that the half-wave potentials of both waves are independent of pH leads them to the assumption that the reductions are not reversible, since for the reaction

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2,$$

the equation for the potential E_{de} at each point of the wave is

$$\begin{aligned} E_{de} &= E_{\frac{1}{2}} + \frac{RT}{nF} \ln \left\{ \frac{[O_2][H^+]^2}{[H_2O_2]} \right\} \\ &= E_{\frac{1}{2}} + \frac{RT}{2F} \ln \left\{ \frac{[O_2]}{[H_2O_2]} \right\} + \frac{RT}{F} \left\{ \ln [H^+] \right\} \\ &= E_{\frac{1}{2}} + \frac{RT}{2F} \ln \left\{ \frac{[O_2]}{[H_2O_2]} \right\} - \frac{RT}{F} \, . \, \mathrm{pH}, \end{aligned}$$

i.e., that a change in pH of one unit should cause a shift of approximately 60 mV in $E_{\frac{1}{2}}$.

These findings of Kolthoff and Miller[15] are in agreement with those of Kern[5] who found an independence of $E_{\frac{1}{2}}$ with pH for oxygen up to pH 11, where the value of $E_{\frac{1}{2}}$ merges with that of the hydrogen peroxide wave, and the two then follow the theoretical course for a reversible couple.

It was stated, however, by Kolthoff and Miller that as the pH dropped the wave for oxygen became drawn out, giving a more symmetrical wave and a straighter log plot. This, according to Meites,[16] is a good indication of reversibility and implies that some measure of reversibility was in fact attained in the reduction of oxygen at lower pH values.

Since the evidence for the reversibility or otherwise of oxygen reduction in neutral or acid solution seemed uncertain, it was decided to investigate the two reductions.

EXPERIMENTAL

In order that one may apply certain polarographic tests to the reduction waves for this purpose, it is first necessary to establish that the limiting current produced by the reduction is, in fact, primarily diffusion-controlled. Various criteria are available, such as the proportionality of limiting current with concentration of depolariser $I_{\text{lim}} = k \, . \, C$ which is one simplified form of the Ilkovic equation. This equation has already been shown to be followed (in Part I of this work) by each reduction wave and thus a strong indication of a diffusion-controlled process was obtained. Further evidence to support this view is the variation of diffusion current with mercury height. For a diffusion-controlled current it can be shown[17,18] that $I = kh^{\frac{1}{2}}$. As can be seen from the Table I this was so over the range studied.

TABLE I

h, *cm*	*I*, *μA* 1st reduction	*I*, *μA* 2nd reduction	$\frac{I_1}{h^{\frac{1}{2}}}$	$\frac{I_2}{h^{\frac{1}{2}}}$
40	1·85	1·45	0·293	0·229
50	2·0	1·60	0·283	0·226
60	2·2	1·75	0·284	0·226

Since, therefore, the limiting currents produced by the two reductions may be taken as diffusion-controlled, further considerations can be taken into account. It can be shown, for instance,[16,17,18] that for a reversible electrode reaction

$$E_{de} = E_{\frac{1}{2}} - \frac{RT}{nF} \log \frac{I}{I_d - I}$$

where E_{de} = the potential of the polarised electrode,
$E_{\frac{1}{2}}$ = the half-wave potential of the depolariser,
R = the gas constant,
T = the absolute temperature
n = the number of electrons involved in the electrode reaction,
I = the current corresponding to a point on the curve at a potential E_{de},
I_d = the limiting current of the electrode reaction,
and F = the faraday.

This, at 25°, reduces to

$$E_{de} = E_{\frac{1}{2}} - \frac{0{\cdot}0591}{n} \log \frac{I}{I_d - I}\,.$$

Thus, for a reversible diffusion-controlled current the plot of E_{de} against $\log \frac{I}{I_d - I}$ will be a straight line of slope $\frac{0{\cdot}0591}{n}$ at 25°.

At the point when $I = I_{d/2}$, $\log \frac{I}{I_d - I}$ becomes zero, and the potential is that of the half-wave potential.

Although a reversible wave will thus give a linear log plot the converse is not necessarily true, although it does indicate some degree of reversibility. If the value of n is known, a better criterion is obtained from measurement of the slope of this plot, since departure from the theoretical slope is a good indication of irreversibility.

When obtaining values to be used in a log plot the following factors must be taken into consideration.

Correction of both I and I_d must be made for the charging current in solution, and care must be taken that the resistance of the polarographic cell is not high enough to cause an appreciable error in measurements of potential through the voltage drop across the cell. If the cell resistance is higher than about 1000 Ω, correction must be made for the potential drop across this resistance.

In the polarograms obtained in these studies the potential drop was negligible, since the cell resistance was of the order of 400 Ω. This, at the maximum current of 2 μA, would cause a potential drop of no more than 800 μV (0·8 mV).

If the reaction studied is a slow one at the dropping mercury electrode, the curve obtained will change if the rate of potential application is changed. Runs were therefore carried out using half the usual rate of voltage application to determine whether any obvious difference in the curve occurred. No significant change in wave heights or half-wave potentials was found.

TABLE II.—$E_{\frac{1}{2}}$ AND 'SLOPE' OBTAINED FROM LOG PLOTS FOR OXYGEN IN 0·1*N* KCl.

Dissolved oxygen, *ppm*	$E_{\frac{1}{2}}$	mV	Slope of log plot	
	I_a	I_b	I_a	I_b
7·82	93	893	0·0732	0·221
5·28	106	873	0·0694	0·208
4·62	95	895	0·0728	0·211
4·62	95	892	0·0663	0·218
3·82	104	905	0·0718	0·255
2·81	85	878	0·0855	0·222
1·56	108	911	0·0892	0·240
Average	98	893	0·0740	0·225

A series of log plots were made of values from curves obtained with solutions of oxygen containing from 1·5 to 8 ppm of dissolved oxygen. Nearly all the plots resulted in straight line relations between E and $\log \frac{I}{I_d - I}$ (Fig. 1), only a few giving indications of a plot formed from two intersecting straight lines, which, according to Kern,[5] is a characteristic of irreversible reactions.

The values of the half-wave potentials obtained from these plots were consistent at each oxygen concentration, without any trend to show the dependence of half-wave potential with depolariser concentration; this, according to Meites,[16] is a good indication of an irreversible reaction.

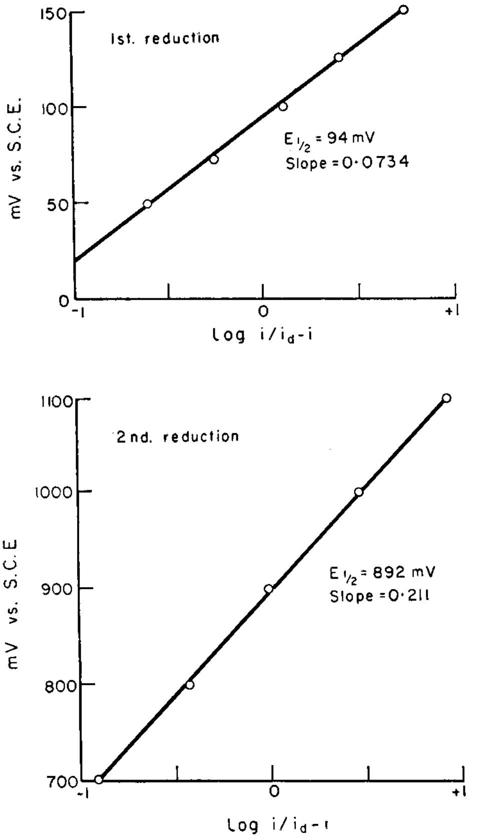

FIG. 1.—Log plots for the reduction of oxygen at a dropping mercury electrode.

The average value for the half-wave potential of the first reduction wave of oxygen in 0·1N potassium chloride solution was found to be 98 mV *vs.* the saturated calomel electrode, while that for the second reduction wave was 893 mV *vs.* the saturated calomel electrode. (Approximate values of 94 and 966 mV were also obtained using a cathode-ray polarograph—see later.) These agree reasonably well with the results quoted by other authors for the same, or similar base electrolytes.

In 0·5N potassium chloride, for example, Giguere and Lauzier[19] found the half-wave potentials to be 70 mV and 820 mV respectively. Kolthoff and Miller[15] gave 50 and 900 mV for the reductions in 0·01N potassium chloride, and Kern[5] gave a value of 65 mV for the half-wave potential of the first reduction wave in 0·05N sodium sulphate. Zuman[20] has found values for the second wave of 940 mV and 1010 mV in acid-base solutions and in neutral base solutions, respectively.

An interesting indication of the relative degree of reversibility of the two reductions of oxygen is obtained by a consideration of the slopes of the log plots for each wave.

As indicated earlier, this slope is equal to 0·0591/n for a reversible reaction at 25°, n being the number of electrons involved in the reaction. For the reductions considered, carried out at 20°, this becomes $\frac{0{\cdot}0581}{n}$ or 0·0291 for each reduction, since both are two-electron processes.[15]

The average values of the slopes obtained over the range of oxygen concentration were 0·0740 for the first, and 0·225 for the second wave, neither slope showing any dependence on oxygen concentration (see Table I).

From these values it can be seen that the first wave is by no means completely reversible, while the second shows a very large degree of irreversibility. The latter is also borne out by the unsymmetrical shape of the second wave.

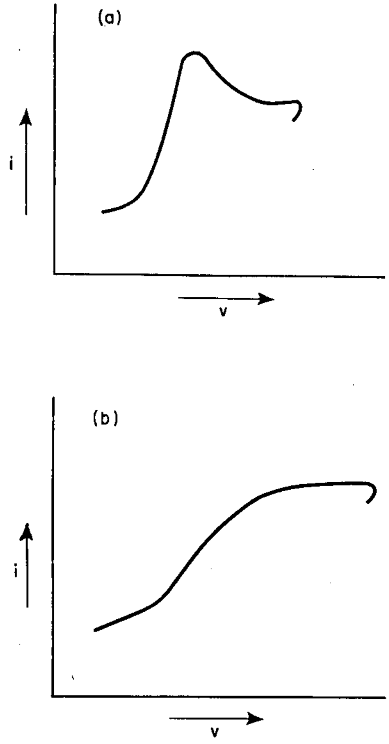

FIG. 2.—Oxygen waves obtained with a cathode-ray polarograph (oxygen in 0·1N KCl)

It has been suggested by Taylor and Smith[21] (quoting Kivalo *et al.*[22]), that for an irreversible reaction the value of $E_{\frac{1}{2}}$ obtained depends upon the capillary used. The values obtained using two electrodes were therefore compared, but no significant difference was found.

Valuable evidence agreeing with the fact that the first wave is relatively reversible, while the second is irreversible, was obtained by the use of a cathode-ray polarograph (by kind permission of Southern Instruments Ltd.).

It was found that the first reduction gave the curves shown in Fig. 2a, while the second reduction gave a very flat wave typical of an irreversible reaction (Fig. 2b).

The first wave gave a good linear plot of peak current against oxygen concentration, the current/concentration ratio being considerably greater (1 μA per ppm as against 0·2 μ A per ppm) than that using a normal polarograph, as is to be expected when using this type of instrument. Since the measurements were carried out using a mercury pool anode, the exact potentials were not known. The anodes hould, however, approximate to a 0·1N calomel electrode, and thus by taking the potential of the anode as being close to this, the half-wave potentials obtained were of the order of 94 mV for the first and 966 mV for the second wave, thus giving results comparable with those obtained with the DC polarograph.

Since the first reduction of oxygen gave a typical peaked curve, it can be assumed that this reduction does in fact possess a high percentage of reversibility. This fact is further confirmed by the evidence from the "Polaroscope Krizik" (by kind permission of Nash and Thompson Ltd.).

Since the potential sweep employed on this instrument is from 0 to −2 V, both reduction waves should show their presence. A typical curve obtained is given in Fig. 3.

The presence of a reversible reaction is shown by a dip or notch in the curve; this is given by the first stage reduction but is rather indefinite for the second. Moreover, if the reaction is wholly reversible a matching notch should appear on the lower wave as the potential returns from −2 to 0 volts.

No secondary notch is seen for the second wave, but one is apparent, though a little displaced, for the first. This shows that the first reaction, while not wholly reversible, is appreciably so, while the second is almost completely irreversible.

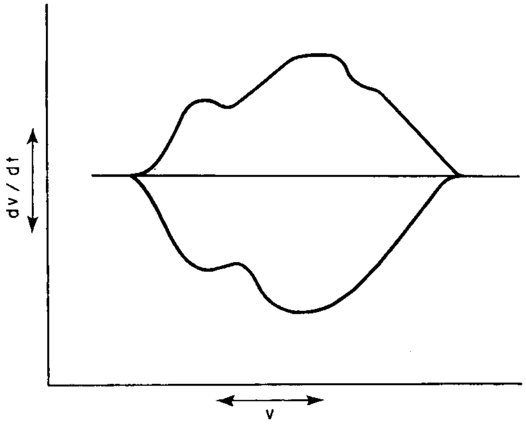

Fig. 3.—Curve obtained for oxygen reduction using the "Polaroscope Krizik".

CONCLUSIONS

Virtually all the tests show the high degree of irreversibility of the second reduction. The first reduction shows a certain degree of non-reversible character, as exemplified by the non-theoretical slope of its log plot, by the non-dependence of half-wave potential with pH, by indications from the cathode-ray polarograph that the half-wave potential alters slightly with oxygen concentration (although no sign of this was shown by the conventional DC polarograph) by the slightly unsymmetrical nature of the "Polaroscope Krizik" curve, and also by the fact that the curve obtained normally with the DC polarograph using an applied potential increasing negatively is not exactly reproduced if the direction of potential increase is reversed. Conversely, indications of a considerable degree of reversibility of the first wave are shown by the fact that a good peaked curve is shown by the cathode-ray polarograph, the peak height being proportional to oxygen concentration (at least over a range of 1 to 10 ppm). This is supported by the occurrence of a notch in the "Polaroscope" $\frac{dv}{dt}\Big/V$ curve and of its corresponding notch when the direction of applied potential is reversed. Further evidence, though of a rather negative kind, is given by the lack of change in half-wave potential with the capillary used, and of the lack of effect of concentration either upon log plot slope or on the half-wave potential obtained from the plot.

Thus it would appear that the first reduction of oxygen dissolved in a $0{\cdot}1N$ aqueous solution of potassium chloride is reversible to a considerable degree but that the second reduction may be considered as virtually irreversible.

Zusammenfassung—Eine Untersuchung der zwei polarographischen Reduktionswellen von Sauerstoff in wässriger Losung wurde durchgefuhrt. Die erste Welle ist zu beträchtlichem Masse reversibel, die zweite nahezu volkommen irreversibel.

Résumé—Les auteurs ont étudié les deux vagues de réduction de l'oxygene en milieu chlorure de potassium. La première vague est réversible, la seconde presque irréversible.

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THE DETERMINATION OF TRACES OF ARSENIC AND ANTIMONY IN SAMPLES OF PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A method is described for the determination of ultramicro quantities of arsenic and antimony in pure platinum. In order to avoid self-shielding differences between samples and standards during neutron irradiation, comparators have been prepared by the addition of very small known amounts of arsenic and antimony to analytical samples. The nuclear reactor BEPO at Harwell has been used as the neutron source; 0·1-g samples of platinum have been taken for the determinations, and a radiochemical separation procedure using carriers has been employed to isolate the induced arsenic and antimony activities.

Results of analyses of seven samples of platinum are quoted. Although contents of as little as 10^{-8} g of either arsenic or antimony were determined, the ultimate sensitivity of the method was not approached.

IN connection with an investigation of the effects of impurities on the electrical and mechanical properties of precious metals, it proved desirable to develop a new neutron-activation method for the determination of traces of arsenic and antimony present in samples of purified platinum.

The nuclear characteristics of arsenic and antimony relevant to activation with thermal neutrons are summarised in Table I. The fact that the half-lives of ^{76}As, ^{122}Sb and ^{124}Sb are 26·6 hr, 2·80 d, and 60·4 d, respectively, made it possible to devise an analysis procedure involving radiochemical separation of first arsenic and then antimony. Because of their short half-lives, 3·5 min ^{122m}Sb, 1·3 min ^{124m}Sb, or 21 min ^{124m}Sb could not be used in the determination of antimony.

It has been estimated[1] that with a thermal neutron flux of 10^{12} neutrons/cm^2/sec, it should be possible under ideal conditions to determine *ca.* 5×10^{-11} g of arsenic, utilising the activated form ^{76}As. The corresponding calculated sensitivity for antimony is 1×10^{-10} g, using ^{122}Sb with ^{124}Sb.

Possible conflicting nuclear processes which may limit the neutron-activation analysis of arsenic and antimony are listed by Koch.[2] However, these do not give rise to interference in the present case.

In order to avoid errors from self-shielding, standardisation has been provided by irradiating similar known quantities *a* and *b* of a sample with very small known amounts of arsenic and antimony mixed with *b*.

EXPERIMENTAL

Irradiation

About 0·1-g samples of platinum, in the form of powdered sponge, were accurately weighed and sealed in silica irradiation tubes of 4-mm internal diameter. Standardisation was provided by the

Table I.—Nuclear data for thermal neutron activation of arsenic and antimony.

Target nuclide	Abundance %	Isotopic activation cross section, *barns*	Product on thermal neutron irradiation	Radiation and energy, *MeV*	Half-life
^{75}As	100	5·4 ± 1·0	^{76}As	β^- 2·97 (50%), 2·41 (31%), 1·76 (15%), 0·36 (3%); γ 0·560, 0·64, 1·20, 1·40, 2·05	26·6 hr
^{121}Sb	57·25		^{122m}Sb	IT γ 0·061, 0·075	3·5 min
		6·8 ± 1·5	^{122}Sb	β^+ (0·01%) 0·565; β^-(97%) 0·74, 0·90, 1·40, 1·97; EC (3%); γ 0·566, 0·686, 1·137, 1·256.	2·80 d
^{123}Sb	42·75	0·03 ± 0·015	^{124m}Sb	IT γ 0·012; β^- 3·2.	1·3 min
		0·03 ± 0·015	^{124m}Sb	IT γ 0·0185; β^- (W) ~ 2·5.	21 min
		2·5 ± 0·5	^{124}Sb	β^- 0·202, 0·36, 0·608, 0·745, 0·871, 0·930, 1·590, 1·658; γ 0·603, 0·632, 0·645, 0·713, 0·722, 0·967, 1·05, 1·33, 1·37, 1·45, 1·70, 2·09, 2·3	60·4 d

addition of weighed portions (*ca.* 0·05 g) of standard solutions of arsenic (20 mg of As/litre, as As^{III} in 2·5*M* HCl) and antimony (20 mg of Sb/litre, as Sb^{III} in 2·5*M* HCl) to 0·1-g samples of platinum in silica irradiation tubes. The liquids were allowed to soak into the metal powder, which was then carefully dried at 70°, after which the tubes were sealed.

Comparators containing the added arsenic and antimony, together with samples to which no arsenic and antimony had been added, were packed with silica wool in standard aluminium screw-top cans and sent to the Atomic Energy Research Establishment, Harwell, for activation. Irradiations were for 1 week in the nuclear reactor BEPO, at Pile Factor 10–12.

Radiochemical separation

Following delivery from Harwell after irradiation, the samples were put through a radiochemical procedure to separate arsenic and antimony radionuclides from interfering activities. Many radiochemical procedures for arsenic and antimony have been described,[3,4] but it was decided to develop a new separation scheme based largely on known solvent extraction behaviour,[5–10] as it was felt that this could be more rapid and convenient than methods involving distillation steps. Ten milligrams of inactive arsenic and 10 mg of inactive antimony were added as carriers, and the radiochemically pure elements obtained from the chemical separations were precipitated for counting as metal and trisulphide,[11] respectively. The chemical yields were determined gravimetrically and were usually about 50% for arsenic and 70% for antimony.

Preliminary experiments with ^{76}As and ^{124}Sb tracers showed that there were no losses of arsenic or antimony by volatilisation accompanying the dissolution of samples.

Preparation of carriers

Arsenic: (10 mg of As/ml). Dissolve 3·30 g of AnalaR As_2O_3 in 20 ml of 2*M* NaOH. Dilute the solution to 100 ml, make it just acid by the addition of 1*M* HCl and transfer it to a 250-ml calibrated flask. Add 2 g of $NaHCO_3$ and when this has dissolved dilute to volume with H_2O.

Antimony: (10 mg of Sb/ml). Dissolve 6·67 g of Analar $KSbC_4H_4O_7$ in H_2O and dilute to 250 ml in a calibrated flask.

The carriers may be conveniently standardised periodically by titrating 5- or 10-ml aliquots with 0·1*N* $KBrO_3$, using *p*-ethoxychrysoidine as a reversible indicator.

Radiochemical separation procedure

Treat each sample in the following manner:

Step 1: Remove a silica irradiation tube from the can, open it at the construction and transfer the contents quantitatively to a 150-ml beaker containing 1 ml of standard As-carrier, 1 ml of standard Sb-carrier, and 5 ml of 12*M* HCl. Wash out the tube thoroughly with warm 6*M* HCl and transfer the washings to the beaker. Heat on a water-bath and add the minimum quantity of 16*M* HNO_3 necessary to dissolve the platinum. Remove HNO_3 by heating with three portions of hydrochloric acid-hydrogen peroxide solution (2 ml of 12*M* HCl and 1 ml of 30% H_2O_2). Add 2 mg of Au (as Au^{III} in 0·1*M* HCl) and evaporate to a volume of 5 ml, with the addition of small amounts of H_2O_2 from time to time. Transfer the solution to a clean 50-ml centrifuge tube.

Step 2: Dilute the solution to 15 ml with H_2O, warm to 80° and add 10 ml of 10% NH_4Cl dropwise with stirring. Cool in ice for 15 min to ensure essentially complete precipitation of $(NH_4)_2PtCl_6$. Centrifuge and transfer the supernate to a clean 50-ml centrifuge tube. To the solution add 0·5 g of $N_2H_4{\cdot}2HCl$ and digest on a water-bath for 10 min to precipitate Au. Centrifuge, and transfer the supernate to a 100-ml separating funnel.

Step 3: To the solution add 10 ml of 12*M* HCl, 10 ml of 18*M* H_2SO_4 and 2 drops of 10% KI solution. Cool and extract As^{III} by agitating with three 10-ml portions of $CHCl_3$. Separate and combine the organic extracts for *arsenic determination* and retain the aqueous phase for *antimony determination.*

Step 4. *Procedure for arsenic:* Wash the organic phase with two 10-ml portions of 6*M* HCl and discard the washings. Transfer the organic layer to a clean 50-ml centrifuge tube. Add 10 ml of 1% $N_2H_4.2HCl$ solution and agitate to extract arsenic into the aqueous layer. Separate the aqueous layer into a clean centrifuge tube and discard the organic phase. To the aqueous solution add 20 ml of 12*M* HCl and 5 ml of 20% $(NH_4)H_2PO_2$. Digest until the precipitate of As coagulates. Centrifuge and discard the supernate. Wash the precipitate with two 10-ml portions of H_2O.

Step 5: Add a few drops of Sb carrier solution and a few drops of Ge carrier (10 mg of Ge/ml as Ge^{IV} in 2*M* NaOH). Digest with 5 ml of 12*M* HCl and 2 ml of 30% H_2O_2 to dissolve the As. Add 10 ml of 6*M* HCl, cool, and extract Sb^V with two 10-ml portions of $(iso\ C_3H_7)_2O$. Separate and discard the organic phases. Make the aqueous phase at least 9*M* in HCl and extract Ge^{IV} with two 10-ml portions of CCl_4. Discard the organic phases.

Step 6: To the aqueous solution add 5 ml of 20% $(NH_4)H_2PO_2$. Digest on a water bath until the precipitate of As coagulates. Centrifuge and wash the precipitate with three 10-ml portions of H_2O. Finally transfer the As with a little H_2O to a weighed aluminium counting tray, evaporate to dryness under an infrared lamp and determine the chemical yield.

Step 7: *Procedure for antimony:* To the aqueous solution from Step 3 add 2 ml of 0·1*N* $Ce(SO_4)_2$ to oxidise Sb^{III} to Sb^V. Extract Sb^V with three 10-ml portions of $(iso\ C_3H_7)_2O$. Separate and combine the organic phases. Wash the combined organic extract with 10 ml of 6*M* HCl and discard the washings. Add 5 drops of 12*M* HCl and evaporate off the solvent. To the residue add 3 ml of 18*M* H_2SO_4 and 1 ml of 1% $N_2H_4.2HCl$, and dilute to 20 ml with H_2O. Add 1 ml of 10% KI and extract Sb^{III} with two 10-ml portions of C_6H_6. Separate and combine the organic layers.

Step 8: Back-extract Sb^{III} from the organic phase by agitating with 10 ml of 6*M* NaOH. Separate the aqueous layer into a clean 50-ml centrifuge tube and dilute to 20 ml with warm H_2O. Add 1 g of $Na_2S_2O_4$ and digest on a water-bath for 10 min. Centrifuge and discard the supernate. Wash the precipitate of Sb with H_2O.

Step 9: Dissolve the Sb in the minimum quantity of 12*M* HCl and 30% H_2O_2. Adjust the acidity of the solution with NaOH until it is only just acid and there is no turbidity. Add 25 ml of a saturated solution of NH_4CNS and digest on a water-bath until the precipitate of Sb_2S_3 coagulates. Centrifuge, and wash the precipitate thoroughly with H_2O before transferring it to a weighed aluminium counting tray. Evaporate to dryness under an infrared lamp and determine the chemical yield.

Measurement of radioactivity

The separated samples of arsenic and of antimony trisulphide were counted under a thin end-window Geiger-Müller counter (EHM 2/S), with associated electronic equipment. All measured

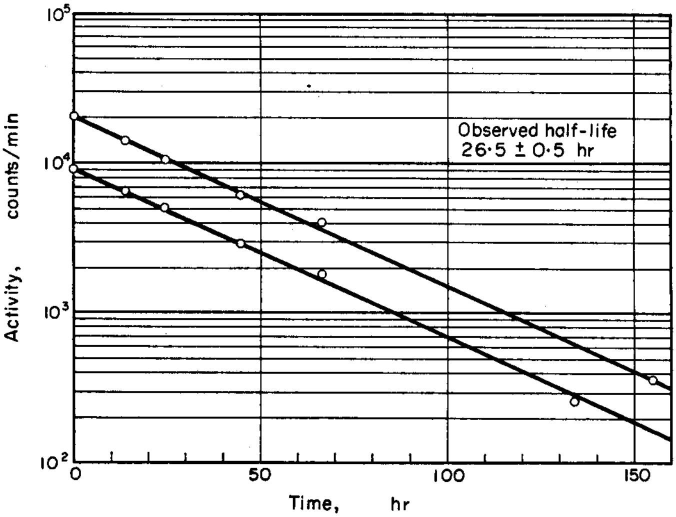

FIG. 1.—Typical decay curves from final precipitates of arsenic.

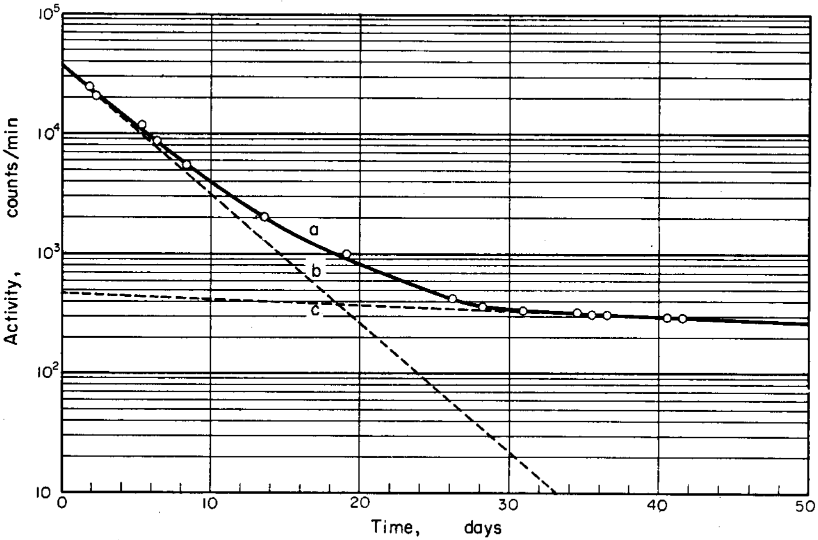

FIG 2.—Part of a composite decay curve from a final precipitate of antimony trisulphide:
(a) Composite decay curve.
(b) Antimony—122 activity (observed half-life, 2·8 ± 0·1 d.)
(c) Antimony—124 activity (observed half-life, 61 ± 2 d.)

activities were corrected for paralysis, background, and chemical yield, and for any decay of significance between measurements on precipitates from samples and comparators. Since the maximum β^--energy of ^{76}As is 2·97 MeV no correction for self-absorption was necessary, and similarly for ^{122}Sb with a maximum β^--energy of 1·97 MeV.

Radiochemical purity of the sources was confirmed by plotting decay curves; typical curves are shown in Figs. 1 and 2.

RESULTS

In Table II are shown results of analyses of purified samples of platinum. The method described in this paper has been applied to samples containing as little as 10^{-8}g

TABLE II.—ARSENIC AND ANTIMONY CONTENTS OF SAMPLES OF PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS.

Sample	Arsenic found, *ppm*	Antimony found, *ppm*
Pt 1	2·75	5·18
	2·99	5·36
Pt 2	2·94	1·19
	2·77	1·26
Pt 3	4·70	0·95
	5·29	1·01
	4·47	0·93
	4·36	0·86
Pt 4	1·18	4·02
	1·15	4·05
Pt 5	0·106	4·03
	0·104	4·02
Pt 6	0·56	0·14
	0·57	0·14
	0·55	0·14
	0·56	0·14
Pt 7	0·71	3·38
	0·76	3·62

of either arsenic or antimony, but even in these cases the ultimate sensitivity of the method was not approached.

Acknowledgment—We are grateful to The International Nickel Co. (Mond) Ltd., for supplying samples of platinum, for financial support, and for a Research Fellowship to one of us (R. A. K.).

Zussammenfassung—Eine Methode zur Bestimmung von Ultra mikromengen von Arsen und Antimon in reinem Platin wird beschrieben. Um Unterschiede in der Selbstabschirmung zwischen Probe und Standard während der Neutronenbestrahlung zu vermeiden, wurden Vergleichsproben bereitet durch Zugabe sehr kleiner aber bekannter Mengen von Arsen und Antimon zu den Analysenproben. Der Harwellreaktor BEPO wurde als Neutronenquelle verwendet. 0.1 g Proben von Platin wurden herangezogen und radiochemische Methoden unter Anwendung von Trägern wurden benutzt, um die induzierten Aktivitäten zu isolieren. Sieben Resultate werden mitgeteilt. Bis herunter zu 10^{-8} g Arsen oder Antimon wurden bestimmt, was aber noch keineswegs die äusserste Empfindlichkeit der Method ist.

Résumé—Les auteurs décrivent une méthode de dosage d'ultramicroquantités d'arsenic et d'antimoine dans le platine pur. Afin d'éviter des différences d'autoprotection entrê les échantillons et les étalons pendant l'irradiation par les neutrons, des comparateurs ont été préparés par addition de très faibles quantités connues d'arsenic et d'antimoine aux échantillons analytiques. Le réacteur nucléaire BEPO de Harwell a été utilisé comme source de neutrons. Les dosages ont été réalisés sur 0,1 g d'échantillons de platine; une méthode de séparation radiochimique utilisant des entraineurs a été utilisée pour isoler les activités induites de l'arsenic et de l'antimoine.

Les résultats d'analyses de sept échantillons de platine sont donnés. Bien que des teneurs aussi faibles que 10^{-8} g. d'arsenic ou d'antimoine aient été déterminées, la sensibilité la plus grande de la méthode n'a pas été atteinte.

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THE ULTRAVIOLET SPECTRA OF CHLORINE AND ITS OXIDES IN CARBON TETRACHLORIDE

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Summary—Chlorine and its oxides (Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7) give ultraviolet absorption spectra in carbon tetrachloride. These spectra can be used for the determination of the compounds.

INTRODUCTION

In connection with a study of the radiolysis of carbon tetrachloride[1] a method was required for the rapid determination of chlorine and chlorine oxides directly in this liquid. None of the methods described so far could be adopted.

Many years ago it was found that gaseous chlorine and its oxides show some absorption spectra in the visible light range.[2] Anbar and Dostrevsky[3] measured the ultraviolet absorption spectra of organic hypohalites in carbon tetrachloride. The spectra of some chlorine oxides in water were also published. Chlorine and chlorine oxides are very soluble in carbon tetrachloride and we have examined the ultraviolet spectra of the solutions and the use of these spectra for determination of the substances.

EXPERIMENTAL

Apparatus

A Zeiss universal spectrophotometer, equipped with a hydrogen lamp BGW and NaCl prism were used for the spectrophotometric measurement, with 1-cm cells at room temperature.

Reagents

Carbon tetrachloride: Lachema n.p. carbon tetrachloride, reagent grade, was saturated with chlorine, washed successively with aqueous sodium hydroxide and water, dried over calcium chloride and distilled. The infrared spectrum showed it to be pure and sufficiently dry.

All other chemicals were reagent grade.

RESULTS

I. *Qualitative comparison of spectra*

Chlorine, Cl_2*:* The spectrophotometric determination of chlorine in carbon tetrachloride can be carried out in the ultraviolet region, as was reported a few years ago.[4] Pure gaseous chlorine was prepared by the decomposition of manganese dioxide with hydrochloric acid; it was dried and purified as usual, and dissolved in carbon tetrachloride. In the range 250–450 mμ chlorine shows a simple absorption curve with a maximum at 320 mμ (Fig. 1.).

Chlorine monoxide, Cl_2O*:* The gas was prepared by leading chlorine over mercury oxide at a temperature of 0°. From the reagent tube it was passed directly into the carbon tetrachloride, so that it was accompanied by chlorine. Fig. 2, Curve 1, shows the spectrum of the mixture; the first maximum belongs to chlorine and two other maxima belong to chlorine monoxide. The higher peak is at 395 mμ and the lower at 415 mμ.

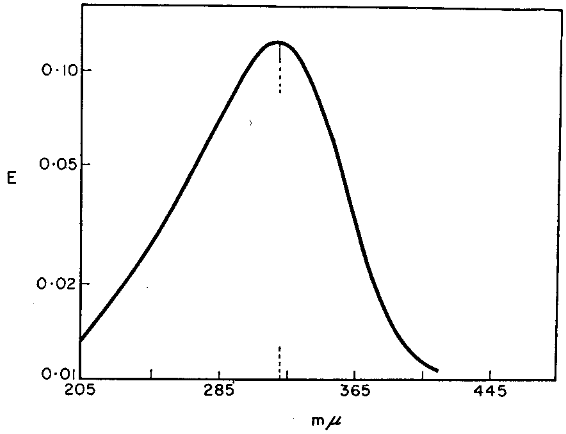

FIG. 1.—Absorption spectrum of chlorine dissolved in carbon tetrachloride.

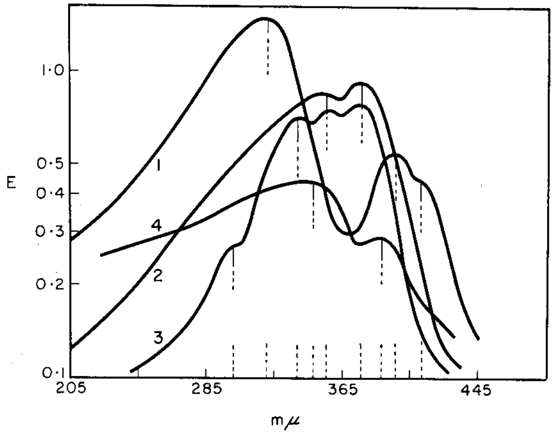

FIG. 2.—Absorption spectra of chlorine oxides dissolved in carbon tetrachloride.
1: $Cl_2 + Cl_2O$; 2: ClO_2; 3: $ClO_2 + Cl_2O_6$; 4: Cl_2O_7.

Chlorine dioxide, ClO_2: The pure compound was prepared by the decomposition of potassium perchlorate with sulphuric acid (in the presence of oxalic acid). Fig. 2, Curve 2, shows the absorption curve, with two maxima, the higher peak at 375 mμ, and the lower at 355 mμ.

Chlorine hexoxide Cl_2O_6: This oxide was prepared by the ultraviolet irradiation of a mixture of chlorine dioxide and oxygen at temperature of 4°. In the vapour form it was bubbled through carbon tetrachloride, and was therefore in solution together with chlorine dioxide. Fig. 2, Curve 3, shows two maxima of chlorine hexoxide. The higher peak is at 340 mμ and the lower at 305 mμ. The other two maxima belong to chlorine dioxide.

Chlorine heptoxide, Cl_2O_7: This was prepared by dehydration of perchloric acid with phosphorus pentoxide, followed by vacuum distillation. Its spectrum is not very characteristic, but this also has two maxima, with wavelengths of 350 mμ for the higher peak and 385 mμ for the lower (Fig. 2, Curve 4).

The wavelengths of the peaks differ so greatly that they can serve as a qualitative criterion, and it is also possible to determine several oxides simultaneously. The dependence of wavelength on the content of oxygen of the oxides may be noted: the wavelengths of the maxima decrease with increasing oxygen-content (with the exception of chlorine heptoxide), as can be seen from Table I.

TABLE I.—WAVELENGTHS OF MAXIMA OF DIFFERENT CHLORINE COMPOUNDS DISSOLVED IN CARBON TETRACHLORIDE

Solute	higher λ_{max}, $m\mu$	lower λ_{max}, $m\mu$
Cl_2O	395	415
ClO_2	375	355
Cl_2O_6	340	305
Cl_2O_7	350	385
Cl_2	320	—

II. *Quantitative determination*

Pure chlorine was dissolved in carbon tetrachloride and its concentration was determined titrimetrically; the solution of chlorine in carbon tetrachloride was shaken vigorously with aqueous ammonia, the aqueous phase was separated, the excess of ammonia was removed by boiling, and the chloride ion content so formed was determined by titration with silver nitrate:

$$3Cl_2 + 6NH_4OH + 2NH_3 = 6NH_4Cl + 6H_2O + N_2 \qquad (1)$$

Other standard solutions were made by appropriate dilutions of this solutions. The extinction was measured at 320 mμ. Fig. 3 shows the calibration curve. It can be seen that the lower limit of determination is about $2 \times 10^{-5}M$, or 1 μg.

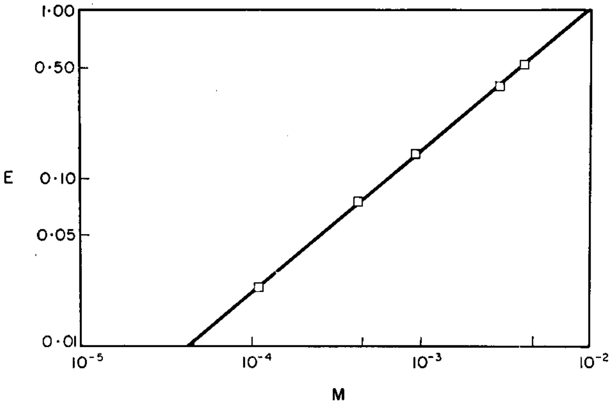

FIG. 3.—Calibration curve for chlorine in carbon tetrachloride at 320 mμ.

For the determination of chlorine monoxide and chlorine dioxide use is made of the effect discovered by Bowen,[2] that both oxides, in carbon tetrachloride, are decomposed by daylight into chlorine and oxygen:

$$2Cl_2O \rightarrow 2Cl_2 + O_2 \qquad (2)$$

$$2ClO_2 \rightarrow Cl_2 + 2O_2 \qquad (3)$$

Through this photolysis the character of the spectra is changed, from those of the oxides to that of chlorine. The determination of chlorine monoxide and dioxide are thus simplified to the determination of chlorine, and the calibration curve for chlorine and the same lower limit apply. The photolysis is complete after about 24 hr, and after that period the chlorine spectra is unchanged. The change in spectrum of chlorine dioxide, for instance, over 24 hr is shown in Fig. 4, after which it was constant.

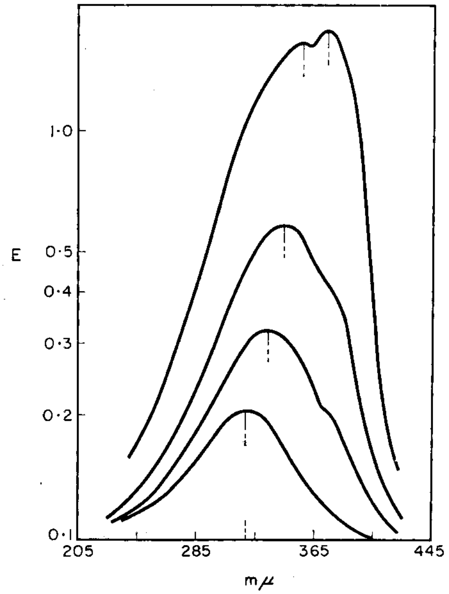

FIG. 4.—Photolysis of chlorine dioxide in carbon tetrachloride. From top to bottom: fresh solution, 1 hr in daylight; 19 hr in daylight; 24 hr in daylight.

From equation (3) the amount of dioxide originally present can be calculated; for chlorine monoxide the procedure is the same. In the presence of chlorine the concentrations are measured before and after photolysis.

Chlorine hexoxide and heptoxide cannot be determined in the same way, since they are not found to be photolysed in carbon tetrachloride. Standard solutions are prepared and measured as for chlorine using the higher peak. The lower limit for their determination was not established.

CONCLUSION

The ultraviolet spectra of chlorine and its oxides, dissolved in carbon tetrachloride, depend on the chemical constitution, are closely related, and can be used for the determination of chlorine, chlorine monoxide, chlorine dioxide, chlorine hexoxide and chlorine heptoxide. Chlorine monoxide and dioxide can be determined as chlorine after their photolysis; chlorine hexoxide, chlorine heptoxide, and chlorine itself, when dissolved in carbon tetrachloride, are not affected by light.

Acknowledgment—Thanks are due to Mrs. J. Šulcová for her technical help.

Zusammenfassung—Es wurde gefunden dass Chlor und seine Oxyde (Cl_2O, ClO_2, Cl_2O_6 und Cl_2O_7) in Tetrachlorkohlenstoff. Absorptionsspektren im Ultraviolett geben, was zur Analyse der Verbindungen herangezogen werden kann.

Résumé—L'auteur a trouvé que le chlore et ses oxydes (Cl_2O, ClO_2, Cl_2O_6 et Cl_2O_7) donnent des spectres d'absorption ultra-violets dans le tétrachlorure de carbone. Ces spectres peuvent être utilisés pour le dosage de ces composés.

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THE INFLUENCE OF THE NATURE OF THE ORGANIC SOLVENT ON THE EXTRACTION OF CHELATE COMPOUNDS

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Summary—The influence of the nature of the organic solvent on the extraction of the thenoyltrifluoroacetonates of Np^{V}, Co^{II} and Ce^{III}, the hydroxyquinolates of Np^{V} and W^{VI}, the acetylacetonates of Co^{II} and Fe^{III}, the 1-nitroso-2-naphtholate of Co^{II}, and some other chelate compounds has been studied. As a rule, "co-ordination-unsaturated" chelates (co-ordination number of the central atom greater than twice its charge, bidentate reagent) are extracted better by ketones, esters, and, particularly, by alcohols; and, normally, are less well extracted by ethers and by hydrocarbons and their halogen-substituted derivatives. The extraction of "co-ordination-unsaturated" chelates can in some cases be favoured by the use of an excess of the reagent. "Co-ordination-saturated" chelate compounds (co-ordination number not greater than twice the charge, bidentate reagent) can be extracted by solvents of extremely diverse nature, including non-oxygen-containing solvents of relatively low polarity. Attention is drawn to the possibility of separating "co-ordination-saturated" and "co-ordination-unsaturated" chelate compounds.

FOR the extraction of the chelate compounds formed by a given reagent with various elements, those solvents are used, as a rule, in which the reagent itself is readily soluble. It is known, for example, that hydroxyquinolates and nitrosonaphtholates are extracted chiefly by chloroform, thenoyltrifluoroacetonates by benzene, dithizonates by carbon tetrachloride or chloroform, and so on. Nevertheless, consideration of only the solubility of a reagent in the organic solvent is insufficient for an understanding of the influence of the nature of the solvent on the extraction of the chelates. There are some data which indicate that the properties of the metal also play an essential role in this.[1–5]

In this paper, the question of the influence of the solvent is considered from the point of view of the co-ordination saturation or unsaturation of the central atom of the chelate compound.

EXPERIMENTAL

Radioactive isotopes with a carrier were used (except for ^{239}Np, which was used without a carrier). The equilibrium concentrations of the elements in the aqueous and organic phases were measured by conventional radiometric methods. Buffer solutions were used to establish the pH; the equilibrium pH was measured by means of a glass electrode. In the majority of cases, the organic reagent was added in the form of a solution in the solvent. The volumes of the organic and aqueous phases were equal (10 ml each) and shaking was carried out in graduated separating funnels for 7 min. Measurements of the volumes of the phases were taken into consideration in calculating the percentage extraction.

RESULTS

The influence of solvents belonging to various classes of organic compounds was investigated. For each solvent, the dependence of the percentage extraction E on the pH of the equilibrium aqueous phase was studied. In all cases, the results of a single extraction are given below.

Chelate compounds of cobalt

The influence of the nature of the solvent on the extraction of the thenoyltrifluoroacetonate and the acetylacetonate of cobalt was studied. Majumdar and De noted that cobalt^{II} was extracted poorly by a benzene solution of thenoyltrifluoroacetone (TTA)[6]. We studied the extraction of cobalt^{II} ($6{\cdot}8 \times 10^{-6}M$) with a $0{\cdot}01M$ solution of TTA in n-butanol, methyl ethyl ketone, benzene, and chloroform. The results obtained are given in Fig. 1. Benzene extracted the TTA—cobalt complex over a very narrow range of pH, and chloroform extracted the complex incompletely. Methyl ethyl ketone and n-butanol extracted the TTA-cobalt complex well over quite a wide pH range (5–8·5).

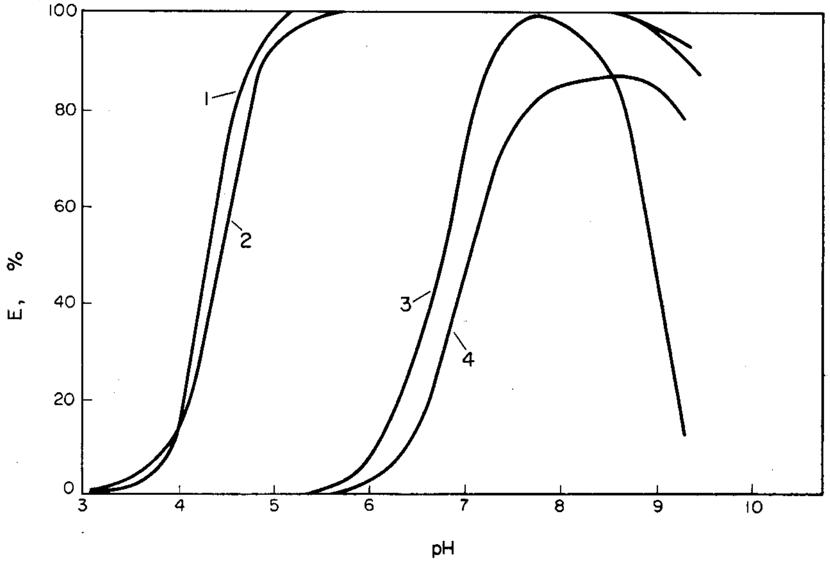

FIG. 1.—Extraction of cobalt^{II} thenoyltrifluoroacetonate: 1—methyl ethyl ketone; 2—n-butanol; 3—benzene; 4—chloroform.

As is well known, the acetylacetonates of bivalent cobalt and nickel are not extracted by chloroform or even by acetylacetone;[2,7,8] methods of separating iron and other elements from cobalt and nickel are based on this. Experiments were made on the extraction of cobalt ($6{\cdot}8 \times 10^{-6}M$) with $0{\cdot}1M$ solutions of acetylacetone in benzene, n-butanol, methyl ethyl ketone, cyclohexanone, and pure acetylacetone. It was found that about 50% of the cobalt was removed in one extraction with n-butanol (pH 8–9). The cobalt was not appreciably extracted by benzene.

The influence of the nature of the diluent on the extraction of the 1-nitroso-2-naphthol-cobalt complex was studied. This chelate compound is extracted to the same extent by both active oxygen-containing solvents and non-oxygen-containing solvents such as, for example, benzene.

Chelate compounds of neptunium^{V} *and uranium*^{VI}

The influence of the nature of the solvent on the extraction of the thenoyltrifluoroacetonate of quinquevalent neptunium[9] was studied in detail. The neptunium was used in indicator amounts (^{239}Np), and the concentration of the TTA in the organic solvents was 0·01*M*. The results are given in Fig. 2. The best solvents for the thenoyltrifluoroacetonate were alcohols—isobutyl, n-butyl, isoamyl, and hexyl. Cyclohexanone and methyl ethyl ketone also extracted neptunium, but not as completely as the alcohols. Neptunium was extracted by esters—ethyl acetate and amyl acetate—approximately as well as by the ketones, or slightly less well. Ethers (di-isopropyl ether), halogen-substituted hydrocarbons (dichloroethane, chloroform, carbon tetrachloride) and hydrocarbons (benzene, heptane), did not extract neptumiun.

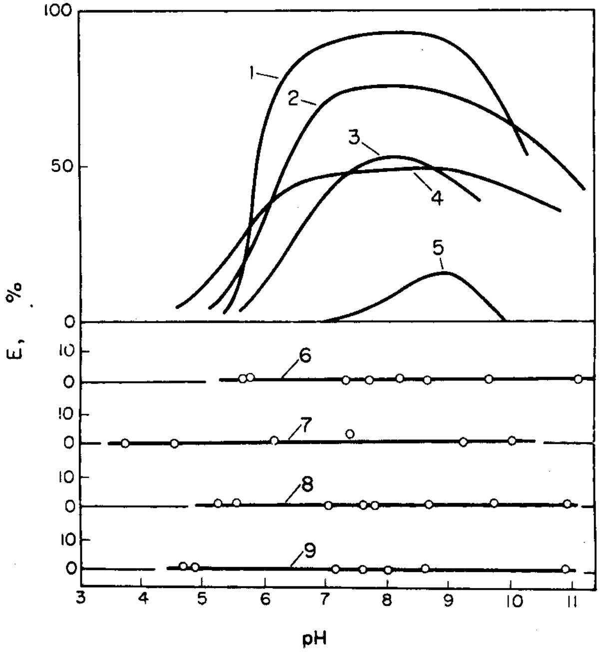

Fig. 2. Extraction of neptunium^{V} thenoyltrifluoroacetonate: 1—isobutanol; 2—cyclohexanone; 3—ethyl acetate; 4—methyl ethyl ketone; 5—amyl acetate; 6—benzene; 7—chloroform; 8—carbon tetrachloride; 9—diethyl ether.

Roughly the same dependence of the extraction of the nature of the solvent was observed in the case of the hydroxyquinolinate and the acetylacetonate of quinquevalent neptunium.

The influence of the nature of the solvent on the extraction of the 1-nitroso-2-naphthol complexes of uranium^{VI} and neptunium^{V} was also studied. It was shown that these complexes are best extracted by alcohols and ketones, and considerably less well by ethers or by hydrocarbons and their halogen-substituted derivatives.

Hydroxyquinolates of thallium^{I} *and thallium*^{III}*

The hydroxyquinolinate of thallium^{I} is extracted well by isobutanol, but is not appreciably extracted by diethyl ether or carbon tetrachloride (initial concentration of

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* In association with V. V. Bagreyev.

thallium in the aqueous phase $3{\cdot}9 \times 10^{-5}M$, concentration of hydroxyquinoline in the solvent $0{\cdot}05M$). See Fig. 3.

The hydroxyquinolinate of thallium^{III}, however, is extracted equally well by alcohols or ketones on the one hand, or by carbon tetrachloride on the other hand.

Chelate compounds of the rare-earth elements and iron

The thenoyltrifluoroacetonate of tervalent cerium (^{144}Ce with carrier) is extracted almost equally completely by isobutyl alcohol, cyclohexanone, and benzene; the extraction of the complexes of the lanthanons and TTA, using a benzene solution of the reagent, has been reported in the literature earlier.[10,11] The acetylacetonate of cerium^{III} is extracted by isobutanol, benzene, and methyl ethyl ketone. The hydroxyquinolinate of lanthanum is extracted to about the same extent by n-butanol and benzene (Fig. 4; it can also be seen that, on the other hand, barium is extracted to a somewhat greater extent by n-butanol).

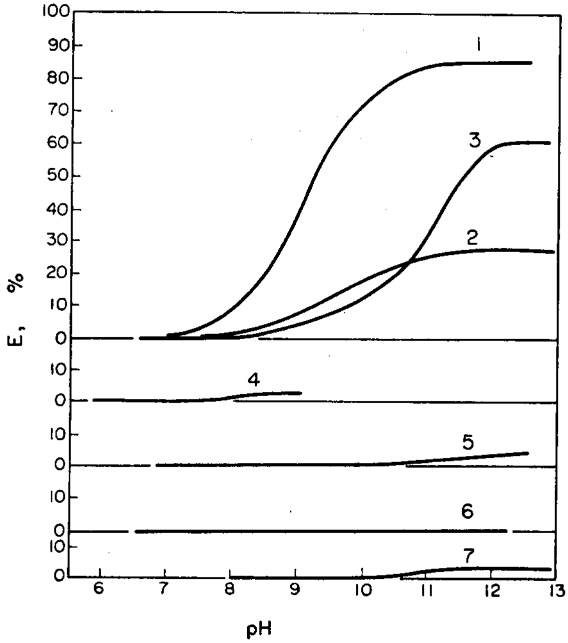

FIG. 3. Extraction of thallium^{I} hydroxyquinolinate: 1—isobutanol; 2—methyl ethyl ketone; 3—chloroform; 4—ethyl acetate; 5—carbon tetrachloride; 6—heptane; 7—diethyl ether.

The acetylacetonate of tervalent iron is extracted to a similar extent by alcohols and by benzene.

Tungsten hydroxyquinolinate

It has been noted earlier that tungsten hydroxyquinolinate is difficult to extract.[5,27,28] The present work has shown, however, that it is only macro amounts of tungsten which are poorly extracted; for example, at a concentration of $(NH_4)_2WO_4$ of approximately $10^{-3}M$, the extraction of the tungsten by benzene or n-butanol at the optimum pH of 5–7 is approximately 30–40%. On the other hand, indicator amounts of tungsten (less than $10^{-7}M$) are extracted well. Several solvents—chloroform, benzene, amyl acetate, methyl propyl ketone, and n-butanol—were investigated. Fig. 5 gives the results for three solvents; the extraction curves for the other solvents are similar. The nature of the solvent, as can be seen from the figure, has practically no influence on the extraction. Minima similar to those which we have described elsewhere[12] can be seen on the extraction curves.

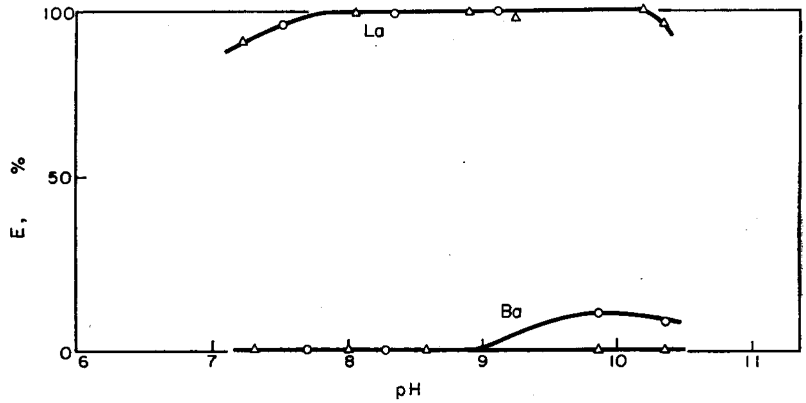

FIG. 4. Extraction of lanthanum and barium hydroxyquinolinates:
○—butanol; △—benzene.

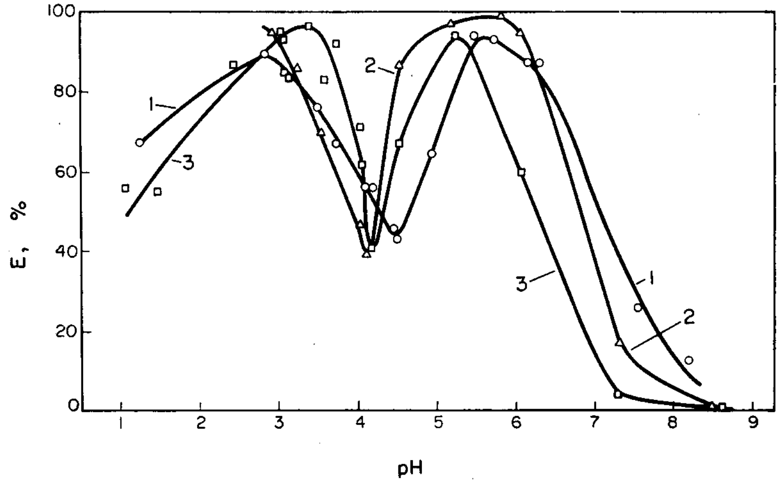

FIG. 5. Extraction of tungsten^{VI} hydroxyquinolinate:
1—n-butanol; 2—chloroform; 3—benzene.

DISCUSSION OF THE RESULTS

The results obtained show that in respect of the influence of the nature of the solvent on their extraction, chelates fall into two groups. The extraction of the chelates of the first group (the chelates of Np^{V}, Co^{II}, Tl^{I}, U^{VI}, Ba) depends quite strongly on the nature of the solvent; these chelates, as a rule, are extracted better by polar oxygen-containing solvents, particularly alcohols, and considerably less well by non-oxygen-containing solvents of low polarity, for example, hydrocarbons and their halogen-substituted derivatives. The dependence of the extraction on the nature of the solvent proves to be very considerable in a number of cases—some chelates are extracted completely by certain solvents and are not extracted at all by others. The chelate compounds of the second group (chelates of Ce^{III}, La, Fe^{III}, Tl^{III}, W^{VI}, Co^{III}) are extracted by solvents of different types—both active oxygen-containing solvents and non-oxygen-containing solvents of low polarity.

The theoretical conclusions reached earlier,[9,13] on the dependence of the extraction of chelates on the co-ordination number of the central atom, are capable of explaining the results obtained.

On the basis of the ratio of the valency and the co-ordination number of the central atom, chelate compounds with bidentate reagents can be divided into "co-ordination-saturated" and "co-ordination-unsaturated" compounds. If the co-ordination number of the central atom does not exceed twice its charge, the chelate compound generally has no free co-ordination positions, and the central atom is completely screened by the ligands ("co-ordination-saturated" chelates); if the co-ordination number of the central atom is more than twice its charge, then the chelate *may* retain free co-ordination positions, which, in the general case, are occupied by molecules of water ("co-ordination-unsaturated" chelates).

The hydrated "co-ordination-unsaturated" chelates are normally extracted poorly. In order to make the extraction effective, it is necessary to displace the water (or "block" it by means of hydrogen bonds) using for this purpose the molecules of some organic substance. Such molecules, in the particular case, may be the molecules of an organic solvent; "active" solvents capable of co-ordination (mainly oxygen-containing solvents) readily displace the water, and they extract "co-ordination-unsaturated" chelate compounds better than "poorly-active" non-oxygen-containing solvents. "Co-ordination-saturated" chelates are capable of being extracted by solvents of extremely diverse types, including "non-active" solvents—*e.g.*, hydrocarbons or their halogen-substituted derivatives.

It can readily be seen that among the chelates which we have studied, those which are characterised by a marked influence of the nature of the solvent on the extraction can be classed as "co-ordination-unsaturated". In aqueous solutions, Np^V forms the cation NpO_2^+, which, it is assumed,[14] has a co-ordination number of six. A co-ordination number of 6 may also be accepted[15] for UO_2^{2+}; a co-ordination number of 6 is also found, in a number of cases, for Co^{II}; Tl^I is capable of exhibiting a co-ordination number of more than two.

On the other hand, the tervalent lanthanons with a co-ordination number of 6 evidently form "co-ordination-saturated" chelates; the "co-ordination-saturated" chelates also include, obviously, Fe^{III} acetylacetonate and the hydroxyquinolinates of W^{VI} and Tl^{III}. The behaviour of Co 1-nitroso-2-naphtholate as a "co-ordination-saturated" compound is a consequence of the fact that, as is well known, in this compound the cobalt is present in the tervalent state (co-ordination number equal to twice the charge). These chelates are extracted by solvents of various types, including benzene. It is obvious that the widespread point of view that the nature of the solvent does not play an essential role in the extraction of chelate compounds is correct only with respect to this particular group of chelates.

In order to ensure the extraction of "co-ordination-unsaturated" chelates, it is desirable to use a pure active solvent which is capable of co-ordination, or which binds water. This solvent can be used as an additive to an inert solvent, for example benzene, and solvents will be suitable for this which cannot be used for extraction in the pure form—*e.g.*, ethyl alcohol, dioxan, acetone, and some amines.[3,4]

In a number of cases, when an excess of the reagent is present, the "co-ordination-unsaturation" of the central atom can be satisfied by the addition of supplementary molecules of the reagent (the formation, for example, of MeR_3^-). When polydentate reagents are used, the free co-ordination positions of the central atom are occupied by the donor atoms present in the molecule of the reagent. In these cases, the chelates may be extracted with inactive non-oxygen-containing solvents—*e.g.*, carbon tetrachloride, *etc.* A tridentate derivative of 8-hydroxyquinoline has been reported which enables calcium to be extracted with chloroform without the addition of primary amines, which favour the extraction of the simple hydroxyquinolinate.[16]

There are a number of cases in the literature which, like the results of these experiments, also confirm these conclusions.

The uranyl ion is predominantly extracted by solvents with a hydrophilic group; this relates, for example, to the complex with TTA.[1] The uranyl salicylate complex is extracted by methyl isobutyl ketone under definite conditions, but is not extracted by chloroform.[17] Besides solvation by the methyl isobutyl ketone, the partial addition of a supplementary molecule of acid also takes place in this case. On extracting the complex of uranium^{VI} with β-isopropyltropolone (HT), in $CHCl_3$ the complex UO_2T_2 (HT) predominates in the organic phase; however, in oxygen-containing solvents, such as methyl isobutyl ketone, the extracted complex does not apparently contain a molecule of HT in excess.[18] The hydroxyquinolinates of the alkaline-earth metals (co-ordination number 6 or 8) are extracted poorly by chloroform, since they contain two molecules of water. These hydroxyquinolinates, however, may be extracted into the organic phase if an excess of the reagent is employed and a solvent capable of co-ordination is used. Dyrssen[21] succeeded in extracting strontium hydroxyquinolinate containing four molecules of oxine per atom of strontium in the presence of a considerable excess of the reagent (about $1M$). Mg[22] and Ca[23] have been extracted when a high concentration of hydroxyquinoline (3%) was used and a co-ordinating solvent—Butyl Cellosolve—was added to the chloroform layer; if the usual conditions for the extraction of hydroxyquinolinates are employed—a 1% solution of the reagent and chloroform as the extractant—Mg, Ca, and Sr are not extracted. Be hydroxyquinolinate is extracted considerably less well by methyl isobutyl ketone than by chloroform.[29] The hydroxyquinolinates of bivalent metals are extracted well in the presence of primary amines (see, *e.g.*, refs. 3, 4, 24). The complex of Sr with perfluorooctanoic acid is not extracted by carbon tetrachloride but is extracted by methyl isobutyl ketone or isopropyl alcohol.[18]

On the other hand, Al hydroxyquinolinate ("co-ordination-saturated" chelate compound) is extracted by benzene, chloroform, carbon tetrachloride, petroleum ether, isoamyl alcohol, and butyl acetate, although best, apparently, by carbon tetrachloride.[25] Sudo[26] obtained similar results. The acetylacetonates of Ni^{II} and Co^{II} are not extracted even by acetylacetone itself, as has already been mentioned;[2] on the other hand, the acetylacetonate of cobalt which has been oxidised to Co^{III} (co-ordination number 6) is extracted well by an excess of the reagent. It is known that many internal complex compounds of quadrivalent elements are extracted by carbon tetrachloride, benzene or chloroform.

Attention may be drawn to the possibility of separating "co-ordination-saturated" chelate compounds from "co-ordination-unsaturated" compounds. The process of separating a pair of cations, one of which yields a "co-ordination-saturated" and the other a "co-ordination-unsaturated" chelate compound with a given reagent, consists in extracting the "co-ordination-saturated" chelate with a solution of the reagent in an inactive solvent—*e.g.*, benzene—at an appropriate pH. Under these conditions, the "co-ordination-unsaturated" chelate compound may, in some cases, remain completely unextracted. Then, sometimes at the same pH, the "co-ordination-unsaturated" chelate is extracted with an active solvent—*e.g.*, butanol—if this is necessary.

We have studied the possibility of separating quinquevalent neptunium and the lanthanons by extracting the thenoyltrifluoroacetonates. Since the pH ranges for the extraction of Np^{V} and, for example, cerium^{III} are similar, it is impossible to separate them by changing the pH. Both thenoyltrifluoroacetonates are readily extracted by isobutanol, but benzene only extracts the Ce.

Acknowledgements—The authors express their thanks to V. V. Bagreyev and G. A. Vorob'eva for their assistance in carrying out the experiments.

Zusammenfassung—Der Einfluss des organischen Lösungsmittels in der Extraktion der Thenoyltrifluoroacetonate von Np^{V}, Co^{II} und Ce^{III}, der Hydroxyquinolate von Np^{V} und Fe^{III}, des 1-Nitrose-2-naphtholates von Co^{II}, und von einigen anderen Chelaten, wurde untersucht. In der Regel werden "koordinationsungesättigte" Chelate (d.h. solche mit Koordinationszahl des Zentralatoms grösser als zweimal dessen Ladung) besser durch Ketone, Ester, und besonders Alkohole, und schlechter durch Äther, Kohlenwasserstoffe und halogenierte Kohlenwasserstoffe extrahiert. In einigen Fällen wird die Extraktion dieser Chelate durch einen Uberschuss des Koordinationsmittels begünstigt. "Koordinationsgesättigte" Chelate (d.h. solche mit Koordinationszahl des Zentralatoms kleiner als zweimal dessen Ladung) werden dagegen durch Lösungsmittel mancher Art, z.B. sauerstofffreie, schwach polare Lösungsmittel, extrahiert. Es wird auf die Möglichkeit hingewiesen, "koordinationsgesättigte" Chelate von den Koordinationsungesättigten" zu trennen.

Résumé—Les auteurs étudient l'influence de la nature du solvant organique sur l'extraction des thénoyltrifluoroacétonates de Np(V), Co(II) et Ce(III), des oxinates de Np(V) et W(VI), des acétylacétonates de Co(II) et Fe(III), du 1-nitroso-2-naphtolate de Co et de quelques autres complexes. Il est montré qu'en regle générale les complexes à coordinance insaturée (indice de coordinence de l'atome central supérieur au double de sa charge) sont extraits préférentiellement par les cétones, les esters et, tout particulierement, par les alcools, tandis qu'ils le sont moins bien par les éthers, les hydrocarbures et leurs dérivés hologénés. L'extraction de ces complexes peut, dans certains cas, être améliorée par l'utilisation d'un exces de réactif. Les complexes à coordinence saturée (indice de coordinence de l'atome central inférieur ou égal au double de sa charge) peuvent être extraits par des solvants de nature très diverse, entre autre par des solvants non oxygénés de polarité relativement faible. Il en résulte des possibilités de séparation des complexes à coordinence saturée et à coordinence insaturée.

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AN I-Q RECORDER AND ITS APPLICATION TO RAPID COULOMETRIC ANALYSIS AND MICRO-COULOMETRY

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Summary—The author recently described a direct-reading current integrator and subsequently improved it into a recording instrument, the I–Q recorder. It can be used not only for coulometric analysis but also for other purposes. The highest sensitivity range is 10 μA; the reproducibility can be assumed to be 0·1%. Integration is possible from input zero to rated value. Rapid determination of micro amounts of copper and lead, 1–10 μg and 4–10 μg respectively, has been carried out. Rapid determination of 0·9 mg of lead and 0·8 mg of cadmium from their mixtures is discussed.

INTRODUCTION

CONTROLLED potential coulometric analysis has been studied by several groups of workers in recent years. Of these studies, a great many are concerned with instrumentation. A possible explanation for this fact is that first, no suitable instrument has been produced; secondly, instrumentation in this field is difficult. Current integration, however, is one of the very important techniques in routine chemical analyses. Besides its application to coulometric analysis, it can be applied to other routine instrumental analyses, such as integration in gas chromatography and intensity integration in spectrophotometry. It can also be applied to research technique in physical chemistry.

In controlled potential coulometric analysis, according to Lingane,[1] the electrolysis current which is integrated decreases exponentially. For the integration of such a current which varies, a suitable integrator is required. Such an integrator can also be used for constant current coulometric titration. However, the current-time technique of constant current coulometric titration cannot be used for controlled potential technique. Thus an integrator for controlled potential coulometric analysis has wide use. Devices which can also be used for both techniques are chemical coulometers,[2] electromechanical integrators[3,4,5] and the method of calculating from the current-time curve.

The author has previously described a direct-reading current integrator[6] which employs a bevel gear differential and a tachogenerator for standardisation. The advantage of this integrator is that it has several good characteristics of which high output power and high sensitivity are the most important. These advantages made possible the development of the I-Q recorder. As previously described in a preliminary report,[7] rapid coulometric analysis can be achieved by using this type of recorder. Because of its high sensitivity, micro-coulometric analysis of samples in concentrations of 10^{-6}–$10^{-7}M$ can be carried out using the same technique as that used for macro-coulometric analysis.

EXPERIMENTAL

Apparatus

The I–Q recorder is basically the same as the integrator used in previous reports.[7] In the direct-reading current integrator, the measured integration of current was recorded digitally. The major difference in this I–Q recorder, however, is that the chart is driven by the measured number of coulombs and the number of coulombs corresponds to the recorded chart length. On this I–Q recorder chart, the horizontal axis (normally the time axis) indicates the amount of electricity, Q. The vertical axis can indicate any type of signal, *e.g.*, pH, potential, current. In the present case, the electrolysis current, i, is indicated on the vertical axis. Therefore, this I–Q recorder chart indicates electrolysis current, i, against amount of electricity, Q. High sensitivity and rather large driving power are requisites for this recorder. To obtain these requisites, an a.c. amplifier is employed. A standard frequency source using a crystal oscillator drives the synchronous motor which supplies one input to the bevel gear differential causing it to rotate at constant speed.

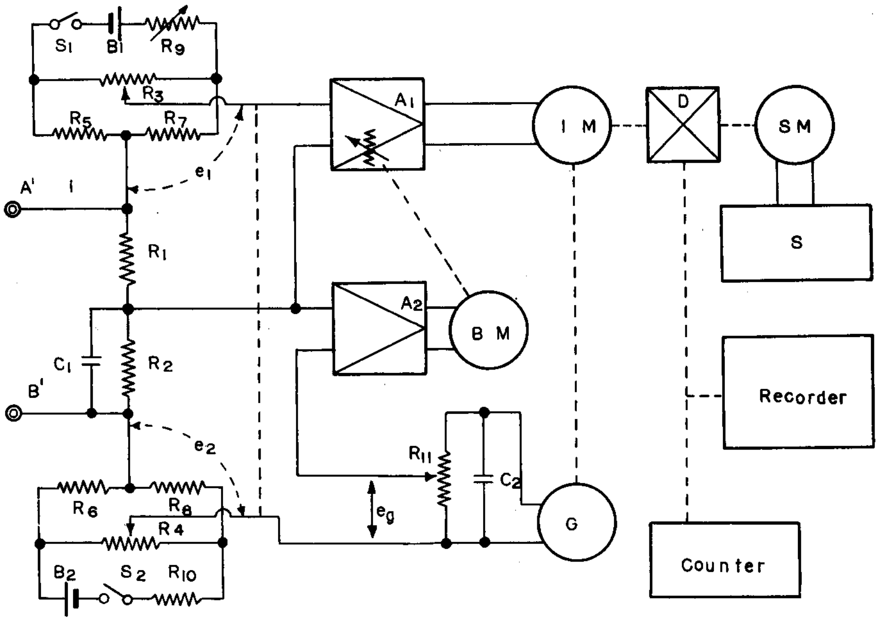

FIG. 1.—Block diagram of coulometer.

A_1:	input amplifier	$R_{1,2}$:	5-kΩ (manganin wire winding)
A_2:	deviation amplifier	$R_{3,4}$:	1-kΩ gang variable resistor
IM:	integrating motor	$R_{5,6,7,8}$:	250-Ω
BM:	servomotor	R_9:	10-kΩ variable resistor
SM:	synchronous motor	R_{10}:	5-kΩ
G:	tachogenerator	R_{11}:	1-kΩ
D:	differential gear	C_1:	10 μF
S:	constant frequency source	C_2:	0·01 μF

Fig. 1 shows a block diagram of the present I–Q recorder. The characteristic curve of the input voltage of IM versus rotating speed is indicated in Fig. 2. Only the linear portion of this curve is utilised by IM. The output axis of the differential gear is mechanically connected to the counter and also to the driving device of the recorder chart. This current integrator circuit can be used to drive many mechanisms requiring rather large driving power. The I–Q recorder was made possible because of this characteristic.

The synchronous motor SM supplies 10 rpm to the differential gear mechanism. When the measured current is zero, the integration motor IM must rotate at 10 rpm. For this purpose, a suitable voltage, e_1, produced by a mercury cell and variable resistor, is always supplied to the input of amplifier A_1 regardless of the measured current. Tachogenerator G, connected to IM by gears, possesses e.m.f. even when the measured current is zero; this tachogenerator voltage is applied to amplifier A_2. Another mercury cell and variable resistor produce a voltage, e_2, which is applied to amplifier A_2 in a similar manner to that in the case of A_1. Here, applied voltage e_2 equals the generated voltage from the tachogenerator when the measured current is zero. For zero adjusting, the voltage of e_1 is changed; similarly, voltage e_2 must be altered accordingly. Under suitable conditions e_1 can be made to equal e_2 by which handling becomes easy. Thus a gang variable resistor is used to keep e_1 equal to e_2 at all times.

To explain further:

$$e_g = KA'(iR_1 + e) \qquad (1)$$

where e_g is the e.m.f. of the tachogenerator, A′ is the amplification factor, i is the electrolysis current, and K is a constant. The voltage of the detective circuit shows

$$iR_2 + e_2 \qquad (2)$$

This device has an automatic control circuit which operates to make equation (1) equal equation (2). From this condition:

$$KA' = \frac{iR_2 + e_2}{iR_1 + e_1} \qquad (3)$$

When i is zero:

$$KA' = \frac{e_2}{e_1} \qquad (4)$$

From equations (3) and (4):

$$\frac{e_2}{e_1} = \frac{R_2}{R_1} \qquad (5)$$

R_1 and R_2 are input resistors and e_1 and e_2 are variable voltages. A gang variable resistor and cells are used to keep ratio R_1/R_2 equal. When K, a ratio of input voltage of the integrating motor and e.m.f. of the tachogenerator, becomes constant, the automatic control circuit does not operate. In the linear condition of the integrating motor, K is constant; however, when the rotation speed of the motor is decreased although the input speed remains unchanged, K becomes smaller and amplification factor A′ of amplifier A_1 must be made larger. Only in this case the automatic control circuit changes amplification factor A′. During good conditions the automatic control circuit need not operate. Consequently the response of this coulometer is good.

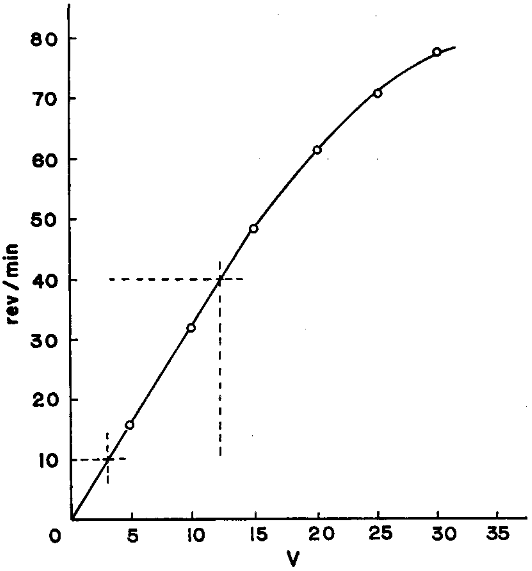

FIG. 2.—Characteristic curve of integration motor.

Tachogenerator

The present apparatus employs a d.c. tachogenerator because the measured current is d.c. and is compared with the e.m.f. of the tachogenerator. A d.c. motor, a battery-clock motor, was used for the tachogenerator.* The internal resistance of this motor was 1 kΩ, and the e.m.f. was 4 mV/1 rpm. The linearity was 0·1 % in the range of 30–120 rpm. The filter circuit was a 0·01-μF condenser which supressed the high frequency noise voltage.

Characteristic of e.m.f. versus revolution of tachogenerator

To measure this characteristic curve accurately, a constant speed motor and gears were used. A synchronous motor was used for the constant speed motor and was supplied by a crystal constant frequency source. Thus the deviation of revolution was within 10^{-3}–10^{-4}%. The gear ratios were changed and the following speeds, 9·885, 19·779, 30·000, 45·498, 60·000, 90·999, 120·000, 181·998 rpm, were used for driving the generator.

Table 1 shows the character of the tachogenerator in the range for actual use and shows e.m.f./1 rpm. To check long-range stability, the measurements were taken on different days, as represented by the numbers in the first column. The standard deviation was under 0·1 %. With regular d.c. tachogenerators, the linearity was 0·25 %; but this tachogenerator has a linearity of 0·1 %, because the revolution range used is narrow. One advantage of this coulometer is that only the range with the best linearity can be used.

TABLE I.—LINEARITY OF TACHOGENERATOR

No. \ rpm	120·000	90·999	60·000	45·498	30·000	mean
1	3·809	3·809	3·813	3·803	3·803	3·807
2	3·808	3·810	3·808	3·803	3·803	3·806
3	3·811	3·811	3·809	3·802	3·802	3·807
4		3·811	3·808	3·807	3·807	3·808
5		3·809	3·813	3·805	3·803	3·808
mean	3·809	3·810	3·810	3·804	3·804	3·807

Numbers in table show mV/rpm.

Integration motor and amplifier

The integration motor requires the following characteristics: (1) Characteristic curve of input voltage *vs.* revolution speed must be linear and long. (2) Inertia of rotor must be small, which contributes to better response. (3) During use, change in motor character must be small. The author used a 2-phase a.c. motor.† Fig. 2 shows the characteristic curve of this motor: input voltage *vs.* revolution speed. The integrating motor of this coulometer has an input voltage in the range of 3·5–12 V. This range is almost linear.

Revolution and its control are performed by the amplifier in Fig. 3. This amplifier requires linearity of input and output voltages. In this condition, integration motor speed is in direct proportion to input voltage. If the character of the amplifier is not linear, the response of the integration motor becomes bad, because motor speed and input voltage are not proportional and time is required to change the amplifier gain. This amplifier has a rated input voltage of 50 mV and uses an output transformer with a primary coil impedance of 5 kΩ and a secondary coil impedance of 500 Ω. The transformer is designed so that the secondary coil impedance is smaller than the control coil impedance of the motor; this improves the motor response.

Constant frequency source

Synchronous motor speed N_s is in direct proportion to frequency f of driving source:

$$N_s = \frac{120}{p} f \quad \text{(rpm)}$$

where p is the number of poles of the motor. A crystal oscillator‡ supplies the standard frequency of this source which has a character of 60 c/sec, 100 V, precision 10^{-5}%.

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* Nippon Denki Tokei Co., Japan.

† Tamagawa Seiki Co., Japan, Type TS 93: output power 3·5 W; 2,700 rpm—no load; exciting current 0·17 A; control current 0·22 A; exciting coil impedance 860 Ω; control coil impedance 680 Ω; gear ratio 1/30.

‡ Toyo Tsushinki Co., Japan, Type TCO–1, natural frequency 12 kc/sec, output frequency 60c/sec by transistor frequency divider.

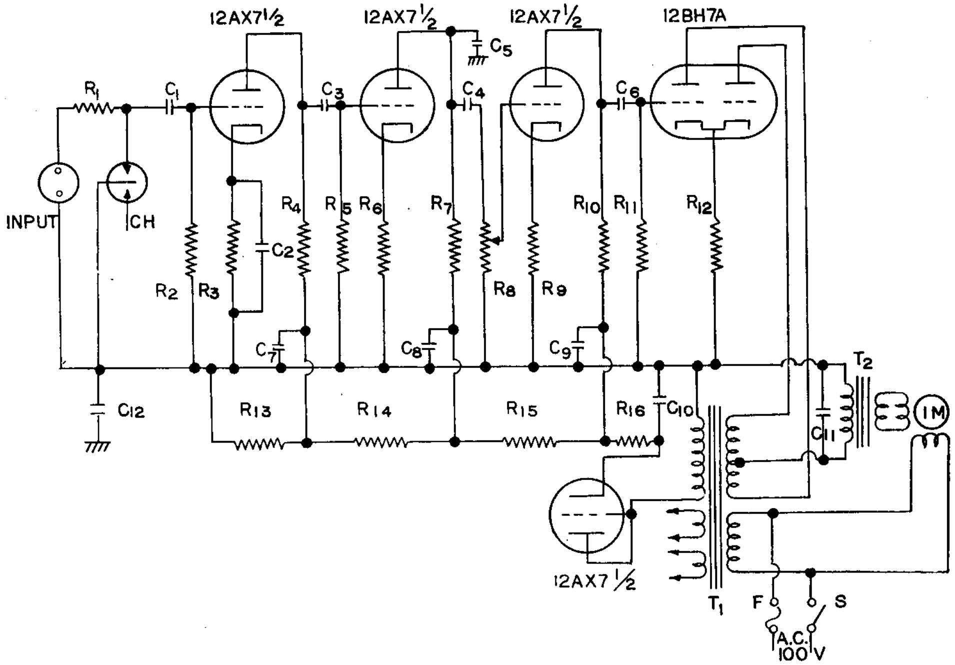


Fig. 3.—Amplifier for integrating motor.

R_1: 1 mΩ
R_2: 500 kΩ
R_3: 3 kΩ
R_4: 500 kΩ
R_5: 1 mΩ
R_6: 20 kΩ
R_7: 500 kΩ
R_8: 500 kΩ
T_1: Transformer
T_2: Output transformer, P. 5 KΩ, S. 500 Ω

R_9: 20 kΩ
R_{10}: 500 kΩ
R_{11}: 500 kΩ
R_{12}: 500 Ω
R_{13}: 200 kΩ
R_{14}: 100 kΩ
R_{15}: 50 kΩ
R_{16}: 10 kΩ

C_1: 0·01 μF
C_2: 10 μF
C_3: 0·05 μF
C_4: 0·05 μF
C_5: 0·01 μF
C_6: 0·1 μF
C_7: 20 μF
C_8: 20 μF
IM: Integrating motor (2 phase, 2 pole)

C_9: 20 μF
C_{10}: 20 μF
C_{11}: 2 μF
C_{12}: 200 μF

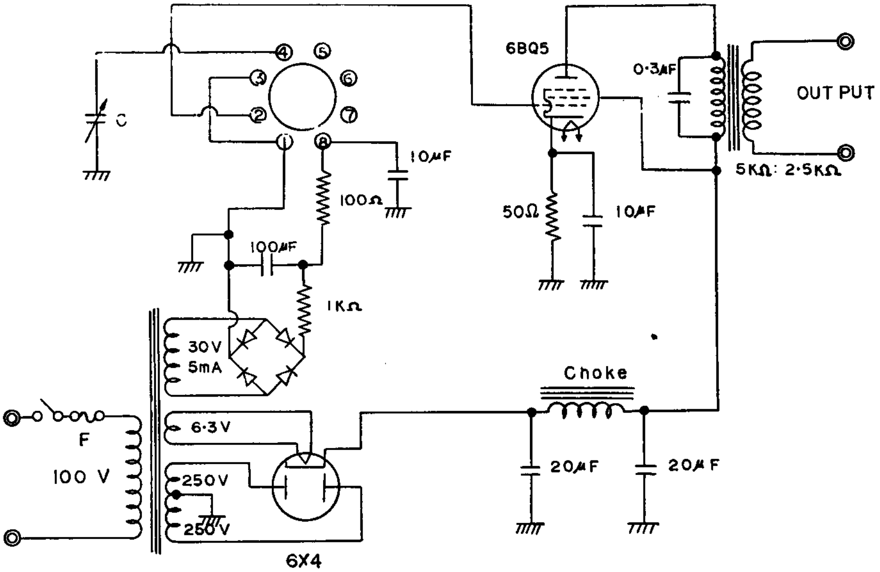


Fig. 4.—Constant frequency source.

Input supplement circuit

The conditions designated in equation (5) must be attained to have this device operate perfectly. Voltage drop iR_1 is supplied to the amplifier and iR_2 is the reference voltage for error detection; R_1 and R_2 do not require absolute values, but these values must be constant. For this purpose, material with low temperature coefficient, manganin wire, is used for the resistors. This coulometer is designed so that the maximum sensitivity of rated current is 10 μA and the maximum input of the amplifier requires about 50 mV; therefore R_1 must be 5 kΩ. R_2 is independent of R_1; but since iR_2 is compared with the e.m.f. of the tachogenerator, the value of R_2 is dependent upon the e.m.f. of the tachogenerator. The ratio of R_1 and R_2 in equation (5) is given an arbitrary value.

To facilitate the making and adjusting of this coulometer, R_1 was made equal to R_2 equal to 5 kΩ. Thus e_1 equals e_2; these voltages must be constant at all times at the set voltage. For this purpose a mercury cell is employed. To drive the integrating motor at 10 rpm, a 20-mV input voltage is necessary and integration is zero at this point. If the electrolysis current contained a background current equivalent to the rated current, e_1 requires -30 mV, *i.e.* -20 mV minus 50 mV. This coulometer is adjusted to a range of ± 40 mV. In general use e_1 requires only 20 mV, but a range from $+40$ to -40 mV is used to facilitate adjusting. By this means:

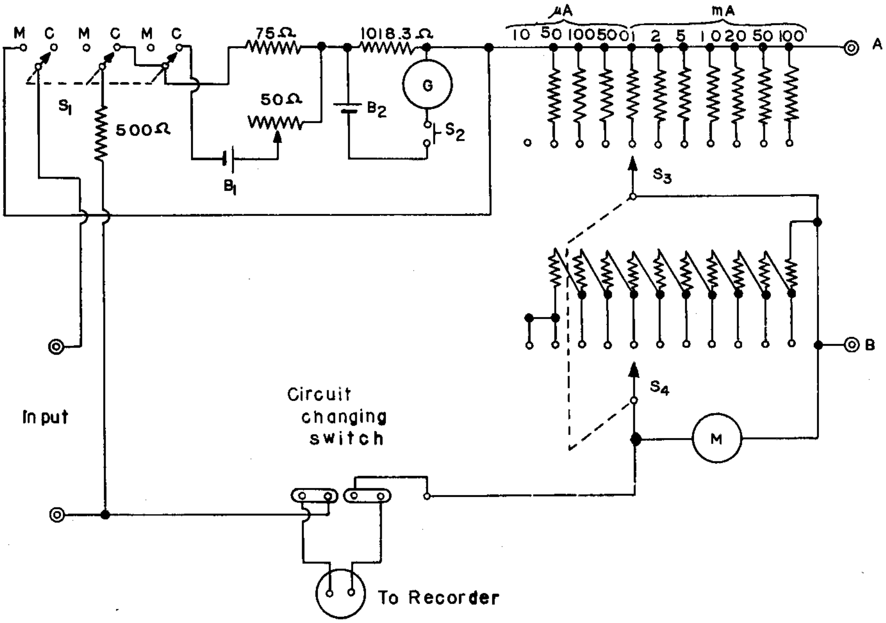


FIG. 5.—Sensitivity change and correction circuit.

electrolysis current $\leqq 2 \times$ value of rated current

provided that

maximum integrated current = value of rated current

maximum non-integrated current = value of rated current.

(background current)

To make e_1 equal to e_2, the angles of rotation of variable resistors R_3 and R_4 must be proportional to their resistances. Generally, the resistances of R_3 and R_4 are difficult to make equal; here, variable resistor R_9 is used for fine adjustment of the difference between R_3 and R_4.

Sensitivity change and correction circuit

Shunt resistors spanning over R_1 and R_2 are used for sensitivity changing. S_3 is an eleven-range switch with the following rated currents: 10 μA, 50 μA, 100 μA, 500 μA, 1 mA, 2 mA, 5 mA, 10 mA, 20 mA, 50 mA, 100 mA. No shunt is used in the 10-μA range. The accuracy of these shunts is not very good, but should be within 0·1–0·05%. Table II shows input voltages for each rated current. This table is used for correction of the shunts. The characteristics of the tachogenerator influence the accuracy of this coulometer, but these characteristics may be changed during long use. The author built-in the null method standardisation circuit in the coulometer. This standardisation circuit consists of a standard cell B(1·0183 mV), standard resistor (1·0183 kΩ), galvanometer G, and produces a 1-mA standardised current. For correction of the coulometer, S_1 in Fig. 5 is switched to C, standardised 1-mA current is passed to the integrating input, the reading is noted and the factor (count/coulomb) is obtained when

TABLE II.—CORRECTION OF SHUNTS

Range	Input voltage,* *mV*	Shunt,† *Ω*
10 μA	100·64	none
50 μA	99·875	2492·9
100 μA	99·263	1101·2
500 μA	100·58	205·30
1 mA	103·59	104·06
2 mA	99·883	50·189
5 mA	100·80	20·200
10 mA	99·927	10·002
20 mA	100·56	5·030
50 mA	100·47	2·009
100 mA	116·08	1·160

* The input voltage is a calculated value and corresponds to the value of rated current times input resistance with shunt.

† This value is calculated from rated current and input voltage.

$$1 \text{ coulomb} = 1 \text{ mA} \times 1000 \text{ sec.}$$

S_3 and S_4 in Fig. 5 are gang switches which change the rated value of meter M simultaneously with the changes in sensitivity at every rated current range except the 10-μA range. When recording the I–Q curve with this device, the circuit changing switch is turned so that the electrolysis current flows to the recorder. To record the amount of electricity versus pH or other signal, the circuit changing switch is turned so that the electrolysis current is cut off from the recorder to which a suitable detector is connected.

Factor

The factor (count/coulomb) should be stable. Table III shows the deviation of this factor in the 1-mA range. Each measured value was taken once or twice each day over 1 month. In the other ranges, the factors are obtained by calculation from the factor of the 1-mA range, then corrected with the values in Table II.

TABLE III.—DEVIATIONS OF FACTOR IN 1-mA RANGE

No.	Factor,* *count/coulomb*
1	$24·99 \times 10^3$
2	$25·04 \times 10^3$
3	$25·09 \times 10^3$
4	$25·00 \times 10^3$
5	$24·98 \times 10^3$
6	$25·02 \times 10^3$
7	$24·97 \times 10^3$
8	$24·99 \times 10^3$
9	$25·00 \times 10^3$
10	$25·01 \times 10^3$
11	$25·02 \times 10^3$

* Mean: $25·01 \times 10^3$; standard deviation: $0·02 \times 10^3$; coefficient of variation: 0·08%.

TABLE IV.—ROUND NUMBERS OF FACTOR IN EACH RANGE

Range	Factor, *count/coulombs*
10 μA	2500×10^3
50 μA	500×10^3
100 μA	250×10^3
500 μA	50×10^3
1 mA	25×10^3
2 mA	$12{\cdot}5 \times 10^3$
5 mA	5×10^3
10 mA	2500
20 mA	1250
50 mA	500
100 mA	250

Recorder

In this device total revolutions of the output axis of the differential gear corresponds to the amount of electricity. This output power moves the counter and the chart-driving mechanism of the recorder. One rotation of output axis corresponds to 1800/17 count; by watching the counter needle, zero adjusting before measurement can be performed precisely. In the chart-driving mechanism, the output power is passed through 1:10 reduction gears in 2 stages to a speed change gear (0·125, 0·25, 0·375, 0·75, 1·5, 3), then through a 40:75 gear train to drive the chart. From these relations, one rotation of the output axis of the differential gear drives the chart for a length of

$$150 \text{ mm} \times 1/100 \times (\text{reduction ratio}) \times 40/75 \text{ (mm)}.$$

One count of the counter corresponds to the chart length of

$$70/2250 \times (\text{reduction ratio}) \text{ (mm/count)}.$$

The starting position of the recording pen can be adjusted to the rated value, *i.e.* electrolysis current minus background current (maximum is rated value) can be recorded.

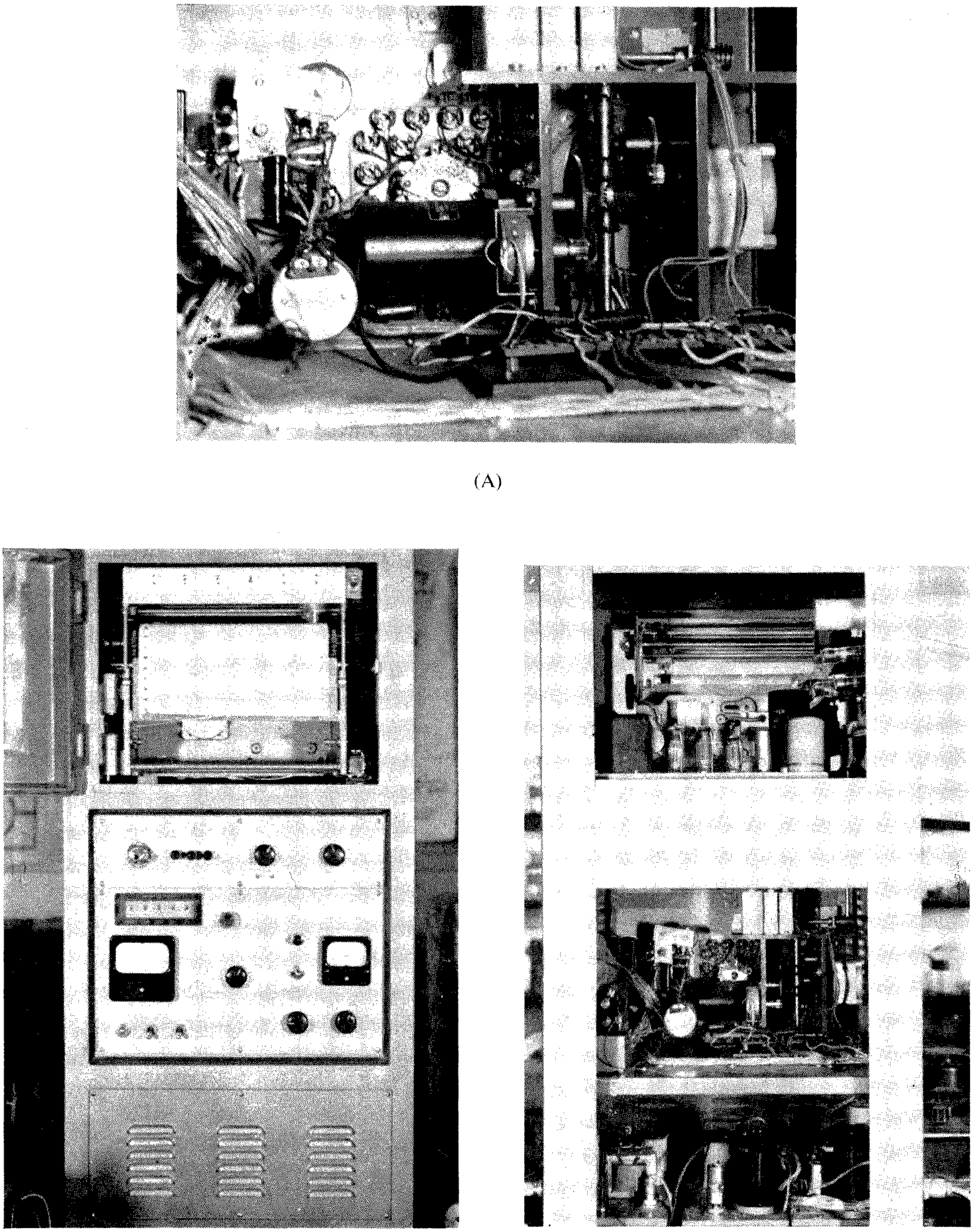
Character of coulometer

Deviation of the factor is 0·08 % (Table III). Linearity of the tachogenerator is 0·1 %. Reproducibility of this device can be assumed to be 0·1 %. When rated input is supplied to the recorder, then cut off, the counter needle moves for a distance of 2–3 counts. When rated input is supplied to the recorder for over 100 sec, the error is under 0·1 %. The counter needle remains stationary for about 20–50 min. The zero shifting (drift) has no effect on the accuracy of this coulometer.

Rapid Determination of Lead and Cadmium

The first step in the experiment concerns the rapid determination of lead and cadmium from their mixtures by means of mercury cathode controlled potential coulometric analysis. Because the deposition potentials of lead and cadmium differ by 0·2 V, their separation from each other is practicable. However, successive determination of each element from one aliquot is not feasible, because the background current varies according to the function of the limited cathode potential. For instance, if after determination of lead, the cathode potential is shifted to the cadmium deposition potential, cadmium is deposited; but, because the background current cannot be measured, this is not a determination. In such a condition, successive determination of each element from one aliquot is possible only if the background current is negligibly smaller than the electrolysis current, or if a condition is found in which background current is reproducible and correction can be made. In these experiments the respective amounts of background current at each cathode potential were found before every determination by pre-electrolysis. In the actual determinations lead alone was determined first, then cadmium plus lead from another aliquot of the same sample, and hence the quantity of cadmium was calculated.

The I–Q curve is a straight line theoretically and experimentally.[7] Therefore, for determination, only the initial short length is sufficient in the recording of an I–Q curve. The inclination of the entire curve is determined by extending a line from this recorded section. By extrapolation, the estimated resultant amount of electricity Q is found at the intersection with the Q-axis.



(A)

(B) (C)

FIG. 6.—(A) Differential gear and main mechanism.
(B) Front view of I–Q recorder.
(C) Rear view of I–Q recorder.

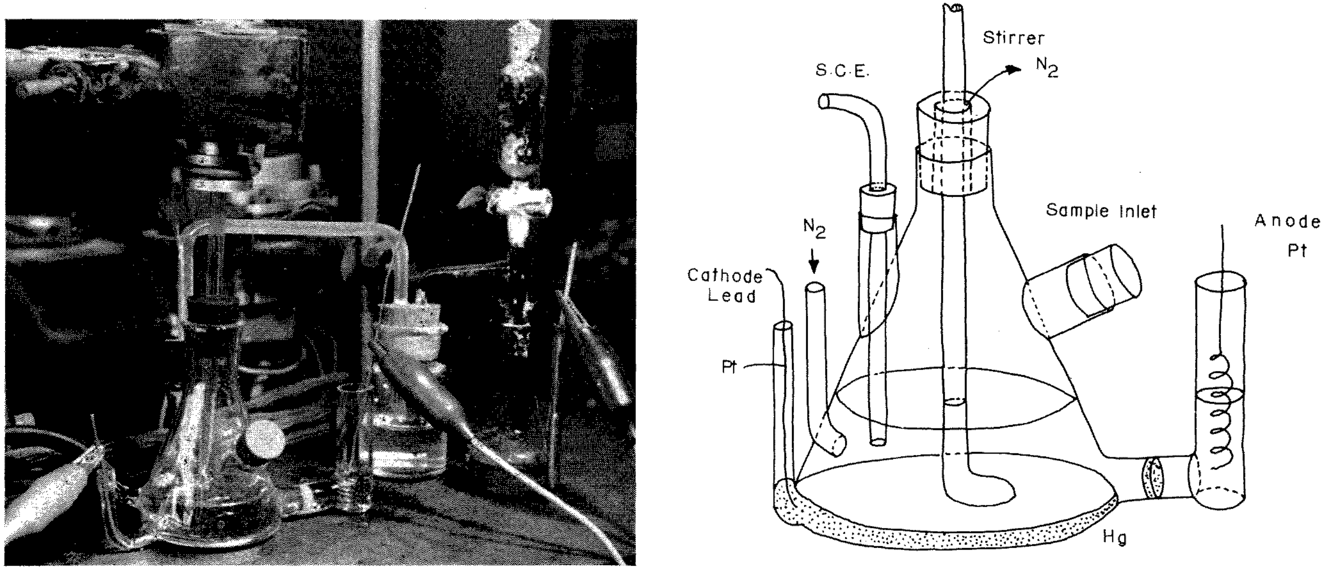


FIG. 7.—Mercury cathode electrolysis cell.

Reagents

Lead and cadmium: Standard samples were made from analytical grade lead and cadmium acetates by electrolysis.

Mercury: Distilled and used for the cathode.

Potassium chloride electrolyte: 0·5*M* potassium chloride (analytical grade) was used for the electrolyte.

Electrolysis cell

Fig. 7 shows a cell used in this experiment. The cathode chamber is made from a 50-ml Erlenmeyer flask to facilitate removal of oxygen. The volume of potassium chloride electrolyte in cathode chamber is 20 ml and in anode chamber 4 ml. The cathode mercury is 10 ml. The spiral anode is 1-mm diameter platinum wire and a sintered glass disk (10 mm diameter) is placed between the anode and cathode chambers.

Potentiostat

The Yanagimoto Seisakusho modification of the Lingane-Jones' potentiostat[10] was used.

Procedure

The cathode chamber was filled with 20 ml of 0·5*M* potassium chloride solution, and the anode chamber with 4 ml of the same solution. The mercury for the cathode, 10 ml, was added to the cathode chamber.

Nitrogen gas was bubbled through the cathode chamber for about 10–15 min before pre-electrolysing. The dissolved oxygen in the supporting electrolyte was reduced at the mercury cathode at about −0·05 V *vs.* S.C.E. Even if the oxygen removal from the supporting electrolyte is incomplete, any remaining dissolved oxygen is reduced during pre-electrolysing; this is possible because the deposition potentials of most substances are more negative than −0·05 V. Because dissolved oxygen present in the sample solution will interfere with the determination, the regular polarographic cell was employed for its removal.

The potentiostat was set at −0·55 V *vs.* S.C.E., 0·5–1 ml of "dummy" sample solution was added to the electrolysis cell, and pre-electrolysis begun and continued till the current (background current) was constant. The reason for this procedure is that the author believes that even when the background current appears constant, a certain small amount of sample remains in the electrolyte under practical conditions. At this time when the background current is constant, the unknown sample is added and the electrolysis continued till the background current again becomes constant, *i.e.* reaches the point of constance at which the unknown sample was added. In this manner the amount of unelectrolysed sample assumed to be remaining in the electrolyte after pre-electrolysing is equivalent to the small sample remaining unelectrolysed after the actual determination. As mentioned above, reproducibility of the background current becomes better, because the electrolysis conditions before and after determinations are about the same.

After this pre-electrolysis, 2 ml of sample solution were added to the cell through the sample inlet. During this addition, care must be taken to prevent the entrance of air. The I–Q curve was recorded till the inclination of the curve could be assumed. A line from the I–Q curve was extended till it crossed the straight line ab (Fig. 8). Point a is the position of the pen just before adding the sample (same position as background current). Straight line ab is parallel to the X-axis. The length of straight line ab corresponds to the amount of electricity for complete electrolysis of the lead. The same procedure was repeated with the cathode potential set at −0·75 V, and the amount of electricity was obtained. This amount of electricity corresponds to the combined amount of lead and cadmium. The amount of cadmium was then obtained by difference.

Table V shows the results of determinations of lead and cadmium.

The values shown are the means obtained from 3–5 determinations. Complete electrolysis ordinarily requires about 2 hr per sample; this rapid method requires only about 30 min per sample. Each determination had a deviation of about 0·01–0·06 mg. These rather large deviations are believed to be caused by a slight error in measurement of chart length.

Determination of Micro Amounts of Copper and Lead

Another advantage of coulometric analysis is its applicability to micro determinations, *e.g.*, the determination of 2–600 mg of copper by controlled potential coulometry using a mercury cathode with an accuracy of 0·1%;[5] determination of $10^{-5}M$ copper using a millicoulometer;[8] determination of $10^{-8}M$ lead using special techniques.[9] Till now the low limit for coulometric determinations has been in the range of 10^{-3}–$10^{-4}M$ (50–100 millicoulomb). The present I–Q recorder can be applied to coulometric determinations in the range of 10^{-6}–$10^{-7}M$. One point which requires careful consideration is the fact that the effect of oxygen during determinations is great. If oxygen is present in the solution in the cell, the I–Q curve shows the presence of oxygen (Fig. 9); thus, it makes possible easy detection of experimental mistakes. This is one of the advantages of the instrument. During micro determinations, current fluctuations, which are rather large when compared with the electrolysis current, are recorded on the chart; this necessitates using a damping circuit (Fig. 10).

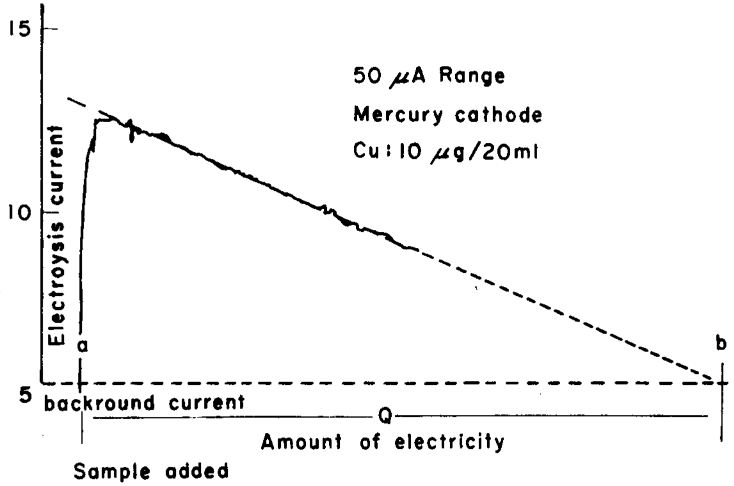


FIG. 8.—Construction of the I–Q curve.

TABLE V.—DETERMINATION OF LEAD AND CADMIUM IN MIXTURES

Sample	Present		Found (mean)		Error		
	mg	*coulombs*	*mg*	*coulombs*	*mg*	*coulombs*	%
Cd[a]	0·798	1·37	0·792	1·36	−0·006	−0·01	0·7
Pb[b]	1·785	1·66	1·815	1·69	+0·03	+0·03	1·7
Pb[c]	0·893	0·831	0·908	0·845	+0·015	+0·014	1·7
Pb + Cd[d]		2·20		2·17		−0·03	
Cd[e]	0·798	1·37	0·772	1·33	−0·023	−0·04	2·8

[a,b] Samples of cadmium and lead alone.

[c] Samples of cadmium and lead in mixtures.

[e] Calculated from (d) minus (c).

Removal of oxygen from sample

Oxygen dissolved in the sample was reduced at the mercury cathode at −0·05 V *vs.* S.C.E., controlled potential electrolysis; therefore, oxygen in the sample must be removed before determination. For this purpose, the author used the apparatus shown in Fig. 11. A 10-mm diameter glass tube with sintered glass bottom was suspended inside a filtering flask. The sample was placed in the glass tube, nitrogen gas was passed in through the side tube and sintered glass, then bubbled through the sample.

If oxygen removal is complete, the I–Q curve is linear[7] and its slope, K, given by:

$$K = \frac{DA}{V\delta}$$

where D is the diffusion coefficient, δ is the thickness of the diffusion layer, V is the total volume of solution, and A is the electrode area. If oxygen removal is incomplete, a bend appears in the I–Q curve as in Fig. 9. The reason for the bend is that the diffusion coefficient of oxygen is larger than the diffusion coefficient of copper or lead; consequently, K of oxygen becomes larger than K of copper

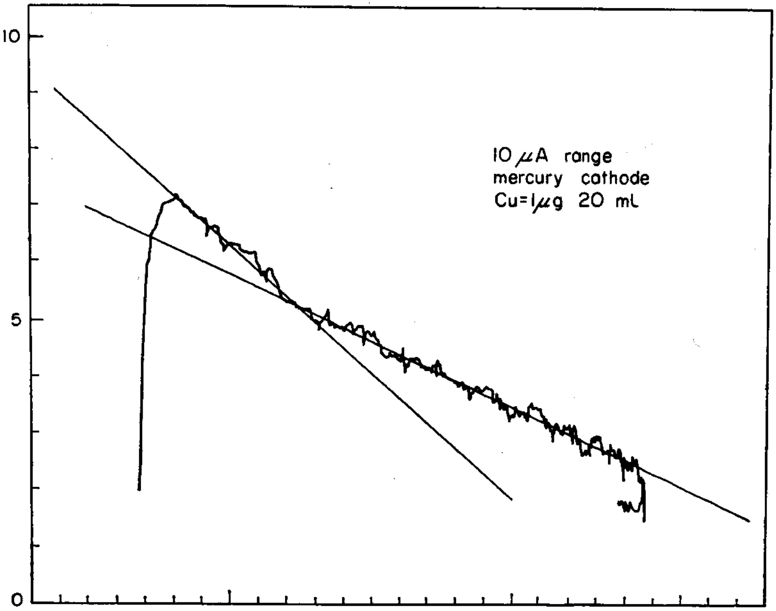


FIG. 9.—Effect of dissolved oxygen.

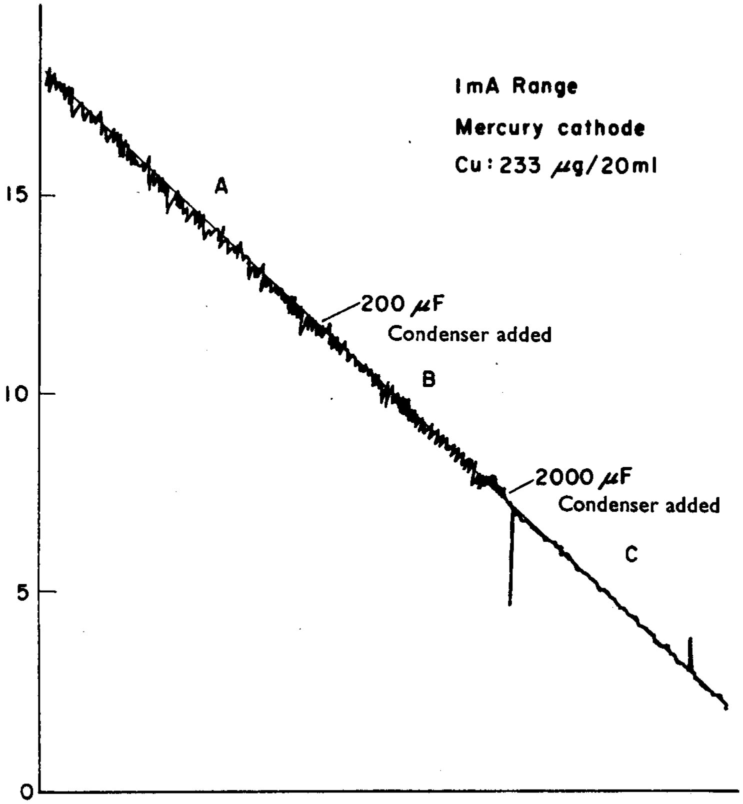


FIG. 10.—Effect of damping circuit.

or lead. Because the effect of oxygen is very great in micro determination, this possibility of checking the oxygen removal from the chart is another advantage of the I–Q recorder.

Damping circuit

Fig. 10 shows the I–Q curve of 233 μg of copper determined at 1-mA range and with mercury cathode; Fig. 12 shows the I–Q curve of 4 μg of lead determined at 10 μA and with mercury cathode. No damping circuit was used when Fig. 12 and the first section of the I–Q curve in Fig. 10 were drawn.

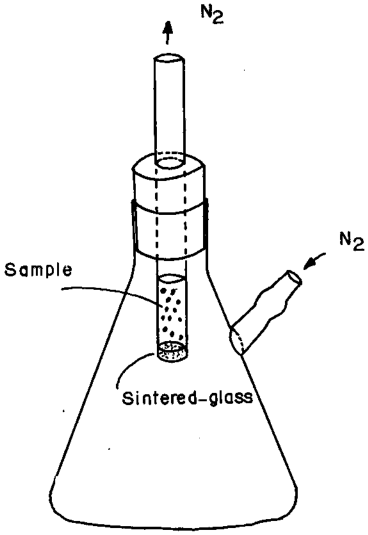


FIG. 11.—Oxygen removal apparatus.

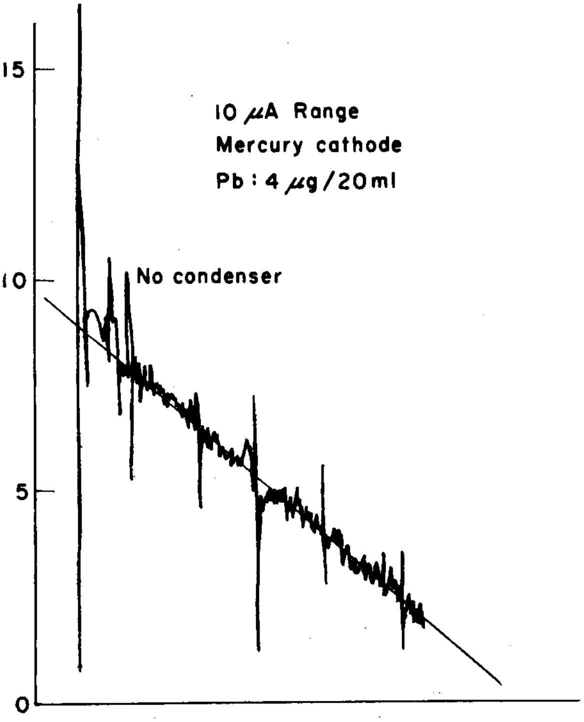


FIG. 12.—I–Q curve with no damping circuit.

In the middle and last sections of Fig. 10, 200-μF and 2000-μF condensers were used, respectively. As the curves show, a damping circuit consisting of a condenser inserted at the terminal of the I–Q recorder is necessary for micro determinations.

The error of the I–Q recorder arising from the addition of the damping circuit is discussed below. The condenser is inserted parallel to the shunt. Because condenser leakage is small in this coulometer, correction is not necessary. Fig. 10 shows the effect of the condenser capacity. Because this I–Q curve remains linear, it can be assumed that the addition of the condenser does not affect the determination. The count/coulomb factor was obtained with and without the condenser, and there was no significance in the factor difference.

Calibration of sampling syringe

To eliminate great change in the 20-ml volume of the electrolyte, a 1·0-ml syringe was used for the 0·5-ml samplings. Another reason for using a syringe was to eliminate oxygen effect. Distilled water was drawn into the syringe and a spacer was inserted between the flanges of the barrel and plunger. The spacer was then removed and the water expelled and weighed. The mean volume was 0·470 ml (standard deviation, 0·001 ml; coefficient of variation, 0·2%).

Electrolysis cell

Fig. 7 shows the electrolysis cell.

Reagents

Copper: A standard solution of copper in the form of $CuSO_4$ was made from 99·99% copper metal.
Lead: The stock solution of lead was made as previously mentioned.

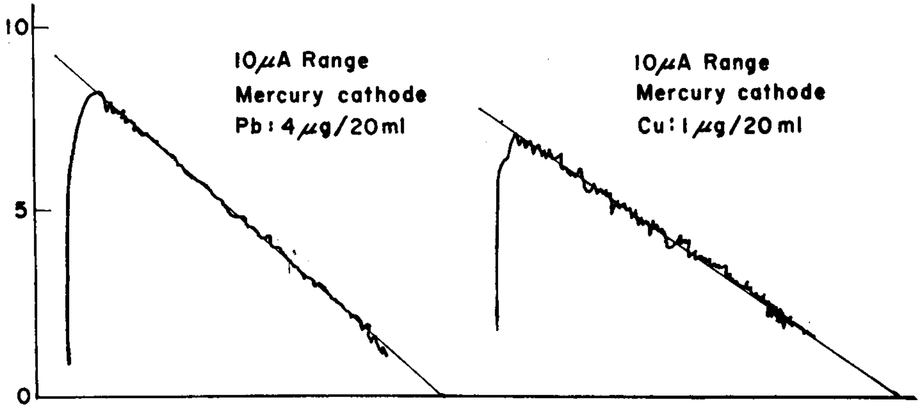


FIG. 13.—I–Q curve for micro determination of lead and copper.

Procedure

Determination of copper: Sample solutions of 2·334 mg/100 ml and 2·33 μg/100 ml were made daily from the stock solution. A sample solution of 2–3 ml was de-oxygenated for at least 1 hr. The electrolysis cell was prepared as above using 0·5*N* hydrochloric acid as supporting electrolyte. The potentiostat was set at −0·34 V *vs.* S.C.E., and the same procedure performed as above. This technique of adding 0·5–1 ml of "dummy" sample solution is particularly important in micro determinations. Equally important is the continual use of nitrogen gas for oxygen removal during determinations. After recording, the chart was constructed, the chart length of Q measured, and the quantity of electricity obtained by multiplying with the factor found from the built-in correction circuit. In this experiment the factor for the 10-μA range was 27·0 mm/millicoulomb and for the 50-μA range 5·36 mm/millicoulomb. The volume of sample measured with the sampling syringe was 0·470 ml and contained 10·97 μg of copper (33·32 millicoulomb) and 1·10 μg of copper (3·33 millicoulomb). The initial current was about 20 μA and 2·5 μA, respectively; the background current was 1·5–3 μA.

Determination of lead: The procedure was the same as that used for copper except that 0·5*M* potassium chloride was used for supporting electrolyte. The potentiostat was set at −0·55 V *vs.* S.C.E. The volume of sample measured with the sampling syringe was 0·470 ml and contained 10·52 μg of lead (9·80 millicoulomb) and 4·21 μg of lead (3·92 millicoulomb). The initial current was about 10 μA and 4 μA, respectively; the background current was 1·5–3 μA.

Figs. 13 and 14 show examples of the I–Q curve of copper and lead when a 2000-μF damping condenser was used.

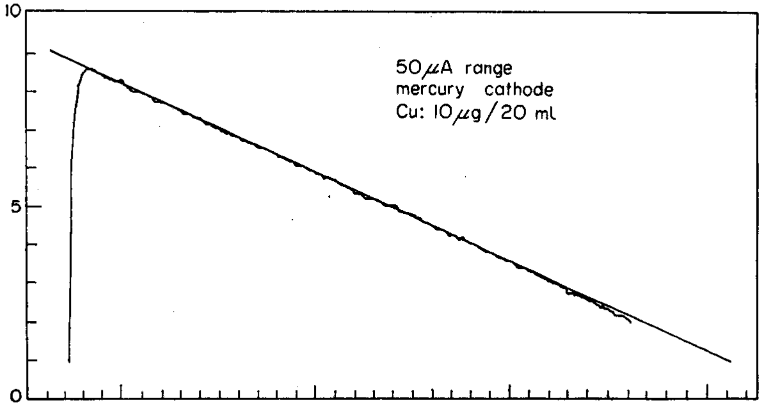


FIG. 14.—I–Q curve for micro determination of copper.

Table VI shows the results of determinations of copper and lead.

The observed values include error introduced during construction of the chart, measurement of the chart length, and other random errors; however, the reproducibility of the determinations is good. When the observed values are compared with the calculated values, the bias is found to be negative and rather large. The results of the experiment show that: (1) The current efficiency seems to be over 100%, but theoretically the current efficiency cannot be over 100%. (2) The I-Q curve is linear in the figure. It can be assumed that there is no side reaction in the electrolysis. (3) Electrical checking proves that this device does not induce these errors. Therefore, it can be assumed that adsorption of the sample on the vessel has a great effect on the determination, because the initial concentration of copper or lead in the electrolyte is very low: $8{\cdot}5 \times 10^{-6}$ and $8{\cdot}5 \times 10^{-7}M$ copper, and $2{\cdot}5 \times 10^{-6}$ and $1 \times 10^{-6}M$ lead.

TABLE VI.—DETERMINATION OF COPPER AND LEAD

	Sample		Found	Std. dev.	Coeff. var.	Error		Range on meter
	μg	*mcoulombs*	*μg*	*μg*	%	*μg*	%	*μA*
Cu	1·10	3·33	1·01	0·02	2	−0·09	− 9	10
	10·97	33·32	10·78	0·09	0·9	−0·19	− 1·7	50
Pb	4·21	3·92	3·65	0·06	1·7	−0·56	−14	10
	10·52	9·80	10·22	0·07	0·7	−0·3	− 3	10

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Zussammenfassung—Der Autor hat jüngst über die Konstruktion eines direkt ablesbaren Stromintagrators berichtet. Das Gerat wurde jetzt zu einem Schreiber erweitert. Das Diagramm zeigt Integration der Stromkurve längs der X-Achse und irgend ein willkürlich gewähltes Signal längs der Y-Achse. In coulometrischen Analysen zeigt die Kurve die Elektrizitätsmenge (Q) auf der X und den Elektrolysenstrom (I) auf der Y-Achse. Daher wird das Gerät I–Q Schreiber genannt. Der höchste Empfindlichkeitsbereich ist 10 μA. Die Reproduzierbarkeit ist zu 0·1 % geschätzt. Integration ist möglich zwischen Null und Höchstwert. Die Schnellbestimmung von Mikromengen Kupfer und Blei (1–10 μg, bezw, 4–10 μg) wurde durchgeführt. Die rasche Bestimmung von 0·9 mg Pb und 0·8 mg Cd in deren Mischung wird diskutiert.

Résumé—L'auteur a récemment mis au point un intégrateur de courant à lecture directe avec appareil différentiel, moteur d'intégration, moteur à vitesse constante, tachygénérateur incorporé comme principaux constituants. Après mise au point de l'intégrateur, l'auteur l'a amélioré ultérieurement sous forme d'un enregistreur. Celui-ci donne l'integration du courant le long de l'axe des X et tout signal arbitraire le long de l'axe des Y. Dans une analyse coulométrique, le diagramme donne la quantité d'électricité Q sur l'axe des X et le courant d'électrolyse I sur l'axe des Y. En conséquence l'auteur a appelé son appareil un enregistreur i–Q. Cet enregistreur peut être employé non seulement pour l'analyse coulométrique, mais encore pour d'autres utilisations instrumentales. Le domaine de plus grande sensibilité est 10 μA; la reproductibilité doit être considérée comme étant de 0,1%. L'intégration est possible du zéro jusqu'à la valeur calculée. Un dosage rapide de micro quantités de Cu et Pb, 1–10 μg et 4–10 μg respectivement, a été réalisé en utilisant enregistreur i–Q. Un dosage rapide de 0,9 mg. de Pb et 0,8 mg. de Cd mélangés est aussi discuté.

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QUANTITATIVE TREATMENT OF EXCHANGE EQUILIBRIA INVOLVING COMPLEXANS—I*

GENERAL CONSIDERATION AND SCOPE OF APPLICATIONS IN ANALYTICAL CHEMISTRY

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Summary—For several cases of practical importance in analytical chemistry, the following exchange equilibrium has been considered theoretically:

$$NY + M + nA \rightleftharpoons MY + NA_n$$

In favourable conditions, the determination of a metal M can be substituted by that of a second metal N using various methods including polarography, photometry, solvent extraction, *etc.* Factors influencing such an indirect determination are discussed in detail. Extending the argument, an equation has been proposed to express the colour change in the vicinity of the equivalence point in the chelatometry M using the NY-A system as indicator. It is possible to find the optimum condition for a given problem if the stability constants of the various species involved in the above exchange equilibrium are available.

INTRODUCTION

BY means of an appropriate exchange reaction, it is sometimes possible to substitute for the determination of one metal that of a second metal which can be more easily determined.[1] Again, when it is difficult to find a suitable metal indicator in the chelatometric titration of a metal, it is often possible to apply a visual titration method using, as an indicator, a system containing a second metal forming a more or less stable chelate with the complexan used and a complexing agent giving rise to a sensitive coloration with this metal.[2-5]

The present paper presents a general discussion of the exchange equilibrium involving a complexan, two metals and a complexing agent. The results are given in a form suitable for application to particular problems of which examples will be given in subsequent papers (see also the preceding paper[6]).

GENERAL CONSIDERATION

The following exchange equilibrium (1) involves two metal ions, M and N, a complexan, Y, and another complexing agent, A† (omitting charges for simplicity):

$$NY + M + nA \rightleftharpoons MY + NA_n \qquad (1)$$

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* Part I—see ref. 6.

† A represents a co-ordinating species, which could be, for example, NH_3 in ammine complex formation, or 8-quinolinolate ion in 8-quinolinolate formation.

Assuming that there is no complex formation of M with A, the equilibrium constant of (1) is written as follows (assuming activity coefficients of unity):

$$K_1 = \frac{[\mathrm{MY}][\mathrm{NA}_n]}{[\mathrm{NY}][\mathrm{M}][\mathrm{A}]^n} = \frac{K'_{\mathrm{MY}}K_{\mathrm{NA}_n}}{K'_{\mathrm{NY}}} \tag{2)*$$

where K'_{MY} and K'_{NY} denote the *apparent* formation constants of MY and NY respectively and K_{NA_n} the overall formation constant of the species of N–A complexes prevailing under the given condition.

From equation (2)

$$[\mathrm{M}] = \frac{[\mathrm{MY}][\mathrm{NA}_n]}{K_1[\mathrm{NY}][\mathrm{A}]^n}. \tag{3}$$

The total analytical concentration of M, N and Y are represented as $[\mathrm{M}]_t$, $[\mathrm{N}]_t$ and $[\mathrm{Y}]_t$, respectively, and are given by equations (4), (5) and (6).

$$[\mathrm{M}]_t = [\mathrm{MY}] + [\mathrm{M}] \tag{4}$$

$$[\mathrm{N}]_t = [\mathrm{NY}] + [\mathrm{NA}_n] + [\mathrm{N}] \tag{5}$$

$$[\mathrm{Y}]_t = [\mathrm{MY}] + [\mathrm{NY}] + [\mathrm{Y}]_t' \tag{6}$$

If we are concerned with sufficiently large values of K'_{NY} and/or K_{NA_n}, the term [N] in equation (5) may reasonably be neglected. In equation (6), $[\mathrm{Y}]_t'$ denoted the total concentration of the complexan not combined with any metal involved. Substituting equation (3) into equation (4), we have

$$[\mathrm{M}]_t = [\mathrm{MY}]\left(1 + \frac{[\mathrm{NA}_n]}{K_1[\mathrm{NY}][\mathrm{A}]^n}\right). \tag{7}$$

(*i*) *If* $[\mathrm{N}]_t = [\mathrm{Y}]_t$

In this case, from equations (5) and (6),

$$[\mathrm{MY}] = [\mathrm{NA}_n] - [\mathrm{Y}]_t'. \tag{8}$$

In order to take into account the amount of NA_n formed in the following equilibrium:

$$\mathrm{NY} + n\mathrm{A} \rightleftharpoons \mathrm{NA}_n + \mathrm{Y}', \tag{9)†$$

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* In the presence of a large excess of a third ligand B, which forms more or less stable complexes with M and N, we should take into consideration the side reaction coefficients β_{M}, β_{N} and $\alpha_{\mathrm{H(Y)}}$, which are defined as

$$\beta_{\mathrm{M}} = [\mathrm{M}]_t'/[\mathrm{M}];\quad \beta_{\mathrm{N}} = [\mathrm{N}]_t'/[\mathrm{N}];\quad \alpha_{\mathrm{H(Y)}} = [\mathrm{Y}]_t'/[\mathrm{Y}]$$

where $[\mathrm{M}]_t'$ and $[\mathrm{N}]_t'$ represent the total concentrations of M and N which are combined neither with Y nor with A, and $[\mathrm{Y}]_t'$ denotes the total concentration of Y not combined with any metals involved. Then it follows that

$$K_1 = \frac{K_{\mathrm{MY}}}{\alpha_{\mathrm{H(Y)}}\cdot\beta_{\mathrm{M}}}\cdot\frac{K_{\mathrm{NA}_n}}{\beta_{\mathrm{N}}}\cdot\frac{\alpha_{\mathrm{H(Y)}}\cdot\beta_{\mathrm{N}}}{K_{\mathrm{NY}}} = \frac{K_{\mathrm{MY}}K_{\mathrm{NA}_n}}{\beta_{\mathrm{M}}K_{\mathrm{NY}}} \tag{2)'$$

where K_{MY} and K_{NY} are the formation constants of MY and NY. In equation (2)′ the following effects are taken into account: protonation of Y, and complex formation of M and N with the ligand B. If M does not form any stable complexes with B, equations (2) and (2)′ become the same, *viz.*,

$$K_1 = \frac{K_{\mathrm{MY}}\,K_{\mathrm{NA}_n}}{K_{\mathrm{NY}}} \tag{2)''$$

In this paper, the absence of such a ligand is assumed unless otherwise noted, and the expression (2)″ will be used for K_1.

† Even in the absence of M, a certain amount of NA_n is formed by equilibrium (9). This amount is equal to $[\mathrm{Y}]_t'$.

Y' representing all species of uncombined complexan. The equilibrium constant for (9), K_2, is given by equation (10):

$$K_2 = \frac{[NA_n][Y]_t'}{[NY][A]^n} = \frac{K_{NAn}}{K_{NY}} \cdot \alpha_{H(Y)}. \tag{10}$$

From equation (10)

$$[Y]_t' = \frac{[NY]}{[NA_n]} \cdot K_2[A]^n. \tag{11}$$

Combining equations (5), (7), (8) and (11), and solving for $[M]_t$,

$$[M]_t = \left([NA_n] - \frac{[N]_t - [NA_n]}{[NA_n]} \cdot K_2[A]^n\right)\left(1 + \frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n}\right). \tag{12}$$

Equation (12) is a general expression for $[M]_t$ when $[N]_t = [Y]_t$.

(ii) *If* $[N]_t \neq [Y]_t$

Combining equations (5), (6) and (11), and rearranging,

$$[M]_t = \left\{[Y]_t - ([N]_t - [NA_n]) - \frac{[N]_t - [NA_n]}{[NA_n]} \cdot K_2[A]^n\right\}$$
$$\times \left\{1 + \frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n}\right\}. \tag{13}$$

These expressions offer a basis for finding favourable conditions for the indirect determination of M, by the polarography or photometry of an equivalent amount of N, and for the chelatometry of M using a system NY-A as an indicator. These will now be discussed in more detail.

INDIRECT POLAROGRAPHY AND INDIRECT PHOTOMETRY OF NA_n IN AQUEOUS SOLUTION

When M is to be determined indirectly by the polarography or photometry of NA_n in aqueous solution, using the exchange reaction (1), a very favourable, though not necessarily an indispensible condition is:

$$[M]_t = [NA_n]. \tag{14}$$

Equation (14) holds provided that

(*a*) $K_2[A]^n$ is sufficiently small in equation (12); in other words, that $[Y]_t'$ can be neglected in equation (8), and

(*b*) the term $\frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n}$ is much smaller than unity in equation (12).

If condition (*a*) is satisfied, equation (12) simplifies to

$$[M]_t = [NA_n]\left(1 + \frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n}\right). \tag{15}$$

From a practical point of view, it may be assumed that equation (14) holds if the second term in the parenthesis of equation (15) is smaller than 10^{-2}. In Table I, the ranges of $[M]_t/[N]_t$ where equation (14) holds for different values of $K_1[A]^n$ are given.

This shows that the greater the value of $K_1[A]^n$, the wider is the range of $[M]_t/[N]_t$ where equation (14) holds. If K_1 is the equilibrium constant for expression (1), given by $K_{MY}K_{NA_n}/K_{NY}$,* it is possible to find a favourable value of K_1 for the determination of M by a reasonable choice of metal N, complexan Y and complexing agent A, *viz.* by an appropriate combination of K_{MY}, K_{NY}, K_{NA_n}. Even after choosing N, Y and A, [A] may be varied to obtain a desirable large value for $K_1[A]^n$. However, it should be noted that since the relationship $K_1/K_2 = K'_{MY}$ always holds, the value of K'_{MY} must be reasonably high to produce a sufficiently high value of K_1 together with a sufficiently low value of K_2.

TABLE I.—RANGES OF $[M]_t/[N]_t$ WHERE EQUATION (14) OR EQUATION (19) HOLDS

$K_1[A]^n$ or $K_3[A]^n$	$[M]_t/[N]_t$
10^4	<0·99
10^3	<0·90
10^2	<0·50

INDIRECT DETERMINATION OF M BY MEANS OF SOLVENT EXTRACTION OF NA_n

To discuss the distribution of the species NA_n between aqueous and organic phases, we consider equation (16):

$$(NY)_w + (M)_w + n(A)_w \rightleftharpoons (NA_n)_0 + (MY)_w, \tag{16}$$

where the subscripts *w* and *o* refer to the aqueous and organic phases, respectively. The equilibrium constant for (16), K_3, may be written as follows:

$$K_3 = \frac{[NA_n]_o[MY]_w}{[NY]_w[M]_w[A]_w^n} = \frac{K_{MY}K_{NAn}}{K_{NY}} \cdot K_D, \tag{17}$$

where K_D refers to the distribution coefficient of NA_n between the aqueous and organic phases. In much the same way as in the preceding section, we obtain

$$[M]_t = [NA_n]_o\left\{1 + \frac{[NA_n]_o}{[N]_t - [NA_n]_o} \cdot \frac{1}{K_3[A]_w^n}\right\}. \tag{18}$$

Equation (18) is quite similar to equation (15). As already mentioned, the higher the value of $K_3[A]_w^n$, the wider is the range of $[M]_t/[N]_t$ where the equation (19) holds (see Table I):

$$[M]_t = [NA_n]_o \tag{19}$$

Now values such as K_D, K_{NA_n}, *etc.*, are not usually known separately. On the other hand, when HA, a weak acid, is used as reagent in the solvent extraction of N, the following relationship is known to hold,[7] as long as the concentration of HA in the organic phase, $[HA]_o$, remains constant:

$$\log D = n(pH - pH_{1/2}) \tag{20}$$

So it might be more convenient to relate $K_3[A]_w^n$ to the pH at the half extraction of N (designated as $pH_{1/2}$) and the pH of the aqueous phase concerned, both of which can be directly determined experimentally.

From the definition of K_D and equation (17)

$$K_3[A]_w^n = \frac{K_{MY}}{K_{NY}} \cdot \frac{[NA_n]_o}{[N]_w}. \tag{21}$$

And if it is assumed that any complexation other than that of NA_n is not appreciable,

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* In the presence of a third ligand B, these constants must be apparent ones.

$[NA_n]_o/[N]_w$ may be regarded as the distribution ratio of N (designated as D) between the two phases. Thus

$$D = \frac{[NA_n]_o}{[N]_w}. \tag{22}$$

Combining equations (20), (21) and (22)

$$\log K_3[A]_w{}^n = \log K_{MY} - \log K_{NY} + n(pH - pH_{1/2}). \tag{23}$$

As seen from equation (23), the values of $K_3[A]_w{}^n$ is determined by a choice of M, N, Y, HA, $[HA]_t$ and the pH at which the extraction is carried out. Therefore by an appropriate choice of these, it is possible to find favourable conditions for the given problem.

CHELATOMETRIC TITRATION OF M USING A SYSTEM NY-A AS INDICATOR

When M is to be determined chelatometrically using a system NY-A as indicator, the condition $[M]_t \gg [NA_n]$ is necessary.* To realise this condition, either of the following two conditions should be satisfied:

(*i*) $[M]_t \gg [N]_t$,
(*ii*) $[M]_t \gg [A]_t$.

We can reasonably confine ourselves to the consideration of the colour change in the vicinity of the equivalence point in these two cases.

(*i*) $[M]_t \gg [N]_t$.

In this case, $[N]_t$ being very small, N should not necessarily be added as NY. However, $[A]_t$ should not be too great when we are concerned with a strongly coloured free indicator or a sparingly soluble one. Accordingly, the consideration of this case is especially useful when one uses a colourless indicator belonging to the first group in the classification[8] by Körbl and Přibil.

Designating the total concentration of complexan used in the titration as $[Y]_t''$, it may be assumed that in the vicinity of the equivalence point $[Y]_t \gg [N]_t$ and $[Y]_t \risingdotseq [Y]_t'' \risingdotseq [M]_t$.

Thus neglecting $[N]_t - [NA_n]$ as compared with $[Y]_t$ in equation (13),

$$[Y]_t''/[M]_t = 1 - \frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n} + \frac{[N]_t - [NA_n]}{[NA_n]} \cdot \frac{K_2[A]^n}{[M]_t} + \frac{1}{K'_{MY}[M]_t}. \tag{24}$$

The last term in equation (24) may reasonably be neglected under the ordinary condition of chelatometry, though it becomes significant in the titration of a very dilute solution, in the case of small K'_{MY}, or at a point very close to the equivalence point.† Thus neglecting the last term

$$[Y]_t''/[M]_t = 1 - \frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n} + \frac{[N]_t - [NA_n]}{[NA_n]} \cdot \frac{K_2[A]^n}{[M]_t} \tag{25}$$

Equation (25) is an expression relating $[NA_n]$ to $[Y]_t''/[M]_t$ in the chelatometry of M with Y. The second term is principally concerned with the colour change before

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* $[NA_n]$ should be reasonably small. To achieve a sensitive colour change with a small $[NA_n]$, the molar extinction coefficient of NA_n should be reasonably large.

† If $K'_{MY} > 10^8$, this term can be neglected except between 100·000% and 100·001% titration of a $10^{-3}M$ solution of M.

the equivalence point, and the third is principally concerned with that after the equivalence point. To achieve a sharp colour change at the equivalence point, the titration should be carried out under conditions where there is a sufficiently large value of K_1 and a sufficiently small value of K_2. If the numerical values of K_1, K_2, [A] and $[M]_t$ are all available, we can determine the colour change in the vicinity of the equivalence point, plotting $[NA_n]/[N]_t$ against $[Y]_t''/[M]_t$. As indicated earlier, K_1 and K_2 being values determined by M, N, Y and A, we can select N, Y and A to obtain favourable values of K_1 and K_2. However it should be noted that there always exists the relation $K_1/K_2 = K'_{MY}$ between K_1 and K_2. Because $K'_{MY} = K_{MY}/\alpha_{H(Y)}\beta_M$, we are able to predict the possible pH range for the titration and the permissable concentration of the third ligand. For the case where $K'_{MY} = 10^{11}$ (*e.g.*, $K_{Ca\text{-}EDTA} = 10^{10.8}$) and $[M]_t = 10^{-3}M$, Fig. 1 shows the plot of $[NA_n]/[N]_t$ against $[Y]_t''/[M]_t$ for various couples of $K_1[A]^n$ and $K_2[A]^n$. Analogous figures can be drawn for each case, and will be useful to predict a favourable condition for a specific problem.

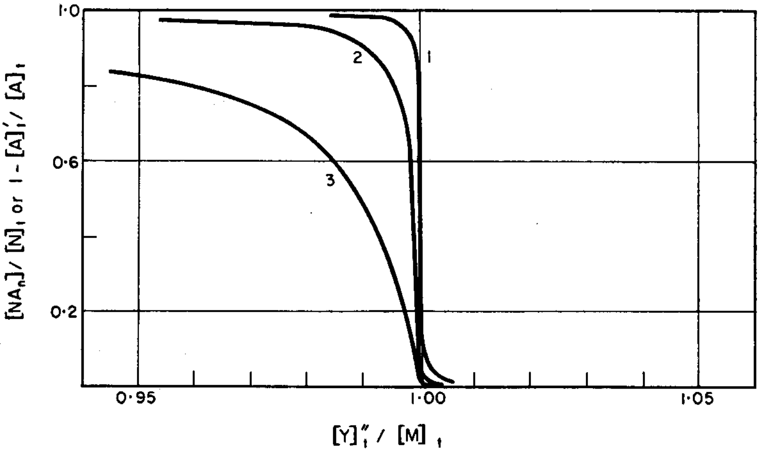

FIG. 1.—Colour change in the vicinity of the equivalence point in the chelatometry of M, using the NY-A system as indicator.

$[M]_t = 10^{-3}M$, $K_{MY} = 10^{11}$

Curve 1: $p = 10^4$, $q = 10^{-7}$;

Curve 2: $p = 10^3$, $q = 10^{-8}$;

Curve 3: $p = 10^2$, $q = 10^{-9}$.

[p and q represent $K_1[A]^n$ and $K_2[A]^n$ respectively in the case (*i*) $[M]_t \gg [N]_t$, and $K_1[NY]/\alpha_{H(A)}$ and $K_2[NY]/\alpha_{H(A)}$ respectively in the case (*ii*) $[M]_t \gg [A]_t$. It is assumed that there is no volume change in the course of the titration.]

(*ii*) $[M]_t \gg [A]_t$.

This is the particular case of a chelatometric titration using a proper metallochromic indicator.[8]

Neglecting [N] in equation (5), from equations (5) and (13)

$$[M]_t = \left([Y]_t - [NY] - \frac{[A]^n}{[NA_n]} \cdot K_2[NY]\right)\left(1 + \frac{[NA_n]}{[A]^n} \cdot \frac{1}{K_1[NY]}\right). \qquad (26)$$

Assuming that N is added as NY, which is reasonably stable in the prevailing conditions, $[Y]_t - [NY]$ is the total concentration of the complexan used in the course of titration. This amount is represented as $[Y]_t''$, as in the preceding section. In the vicinity of the equivalence point, $[M]_t \fallingdotseq [Y]_t''$. Thus, neglecting the last term as before

$$[Y]_t''/[M]_t = 1 - \frac{[NA_n]}{[A]^n} \cdot \frac{1}{K_1[NY]} + \frac{[A]^n}{[NA_n]} \cdot \frac{K_2[NY]}{[M]_t} \cdot \tag{27}$$

Assuming that A does not form any complexes other than the 1:1 complex NA,*

$$[Y]_t''/[M]_t = 1 - \frac{[NA]}{[A]_t'} \cdot \frac{\alpha_{H(A)}}{K_1[NY]} + \frac{[A]_t'}{[NA]} \cdot \frac{K_2[NY]}{\alpha_{H(A)}[M]_t} \tag{28}\dagger$$

where $\alpha_{H(A)} = [A]_t'/[A]$ and $[A]_t'$ denoted the total concentration of A not combined with N. In the titration of M we can find favourable values of K_1 and K_2 by an appropriate choice of N, Y, and A. Moreover for a certain set of K_1 and K_2, [NY] and pH are important factors in deciding the experimental procedure for a given problem (see Fig. 1).‡

Zusammenfassung—Das folgende Austauschgleichgewicht ist in verschiedenen analytischen Problemen von praktischer Bedeutung und wurde theoretisch behandelt;

$$NY + M + nA \rightleftharpoons MY + NA_n$$

Unter günstigen Bednigungen kann die Bestimmung des Metalles M durch die eines zweiten Metalles N ersetzt werden wie z.B. in polarographischen, spektrophotometrischen, extraktiven und anderen Bestimmungsverfahren. Die Faktoren, welche solch eine Bestimmung beeinflussen werden im Detail studiert. Eine Formel wird abgeleitet, die es gestattet den Farbwechsel im Bereich des Aquivalenzpunktes von chelatometrischen Titrationen zu bestimmen wenn M titriert und das System NY-A als Indicator verwendet wird. Die Ergebnisse der vorliegenden theoretischen Untersuchungen gestatten die Berechnung der optimalen Bedingungen, vorausgesetzt die Stabilittäskonstanten der verschiedenen Komplexe sind bekannt.

Résumé—En raison de son importance pratique en chimie analytique la réaction d'échange:

$$NY + M + nA \rightleftharpoons MY + NA_n$$

a été étudié au point de vue théorique. Lorsque les conditions sont favorables le dosage d'un métal M peut être remplacé par celui d'un second métal N en utilisant des méthodes variées comme la polarographie, la spectrophotométrie, l'extraction, etc.

Les facteurs qui influencent une telle détermination indirecte sont discutés en détail. Une équation est proposée qui exprime le changement de coloration au voisinage du point équivalent dans le dosage complexométrique de M en utilisant le système NY-A comme indicateur. A partir des résultats obtenus, il est possible de déterminer les conditions optimales pour un problème donné, dans la mesure où l'on connait les constantes de stabilité des différentes espèces chimiques mises en jeu dans la réaction d'échange considérée.

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[*] In chelatometry, using MgY-Erio T system as indicator, a 1:1 complex is known to be formed. In cases where higher complexes have to be taken into consideration, $[A]_t'$ affects the colour change and equation (28) becomes more complicated. A quantitative treatment of these cases will be published in near future.

[†] $[A]_t' = [A] + [HA] + [H_2A] + \cdots + [H_jA]$. The colour of the dissociated form A often resembling that of NA, another indicator or condition is preferably to be sought, if [A] can not be neglected.

[‡] Where there is also present a third ligand, which forms a reasonably stable complex with N but not with M, its influence appears in the diminution of [NY], of which the degree is dependent on the value of $[Y]_t''/[M]_t$, and hence the colour change becomes obscure [*cf.* equations (2)′ and (28)].

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THE POLAROGRAPHY OF SILVER

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Summary—A true polarographic wave for silver may be obtained in a cyanide medium from which the excess of unreacted cyanide ion is removed by addition of excess of nickel ions. None of the common anions interferes, even thiosulphate, nor do any of the metals examined except Tl^+. The coincident wave of Pb^{2+} may be removed to more cathodic potentials by addition of excess of ethylenediaminetetra-acetic acid.

SINCE silver is more noble than mercury, especially in dilute amalgams, and since both metals form complexes of similar stabilities with the same ligands, it is usually impossible to determine the true half-wave potential of silver ion or its complexes at a dropping mercury electrode. The true reduction potential of silver from most supporting electrolytes is more positive than the potential at which anodic dissolution of mercury begins, and consequently it is only possible to observe a diffusion current due to silver ion and it is practically impossible to observe a full polarographic wave. This type of analytical method has been used in an alkali nitrate or perchlorate medium. The diffusion current under these conditions and with a mercury pool anode is observed at zero applied potential.

Consequently, in order to obtain a fully defined silver wave a complexing agent must be used which forms a more stable complex with silver ions than with mercury^{I} or mercury^{II} ions and which thus shifts the reduction potential of the silver ion to a more negative potential than the mercury wave. An examination of the literature relating to stability constants reveals that few such accessible ligands exist and consequently an alternative procedure must be found.

In our preliminary experiments we examined several common inorganic ligands well known to form powerful complexes with silver ion, *e.g.*, iodide [AgI_4^{3-}, $\beta_4 \approx 15$], thiosulphate [$Ag_2(S_2O_3)_2^{2-}$, $\beta_2 \approx 13$], thiocyanate [$Ag(SCN)_4^{3-}$, $\beta_4 \approx 11$] and cyanide [$Ag(CN)_2^-$, $\beta_2 \approx 21$]. All four ligands form somewhat more stable complexes with mercury ions than they do with silver, however. It is therefore necessary to remove the excess of the complexing agent from the silver solution before carrying out polarography. Thus it has previously been shown that it is possible to obtain a well defined silver wave at the dropping mercury cathode when a pure solution of potassium argentocyanide is used.[1] Unfortunately, whilst this is of academic interest it does not furnish a practicable method for the analysis of dilute silver solutions by polarography.

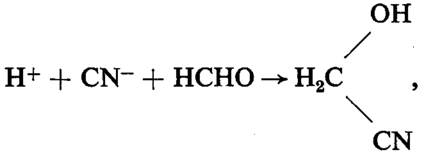
We therefore examined three main possibilities for the removal of excess of complexing agents. The first of these was based on removal by shaking with an excess of insoluble substance which will remove complexing agent without breaking down the silver complex. Thus for iodide ion, with mercuric oxide, the appropriate reaction is:

$$4I^- + HgO + H_2O \rightleftharpoons HgI_4^{2-} + 2OH^-$$

The second method involved addition of another metal ion capable of binding the excess of complexing agent in a soluble complex without breaking down the silver complex. Thus nickel ion may be used to remove an excess of cyanide ion:

$$4CN^- + Ni^{2+} \rightleftharpoons Ni(CN)_4^{2-} \quad (\beta_4 \approx 16)$$

The third method involved destruction of the excess of complexing agent or binding it in a non-reactive form. Thus cyanide ion can be bound as cyanhydrin, since the product formed,



$$H^+ + CN^- + HCHO \rightarrow H_2C\begin{matrix} OH \\ CN \end{matrix},$$

is not reducible at the dropping mercury electrode.

It was found that the first method was not successful because the equilibrium was attained before removal of all the complexing agent. When the method was used on a continuous-removal basis (*i.e.*, in column form) reaction also took place with the silver complexes. Accordingly, attention was restricted to the second and third methods. The latter method is most easily applied to cyanide ion, which is one of the most powerful complex formers for silver ion.

A $10^{-3}M$ potassium cyanide solution in a $10^{-1}M$ potassium nitrate base electrolyte was found to give an anodic wave for the cyanide ion at —0·45V against a calomel element immersed in $10^{-1}M$ KNO_3 and connected to the solution *via* a bridge containing the same electrolyte. When silver was added to a similar solution in amount sufficient to leave a slight excess of free cyanide ion, the polarogram showed a half-wave potential at —0·55V, with a pronounced maximum at *ca.* —0·75V. The maximum was readily removed by the addition of a suppressor such as methyl red. The wave obtained in its presence was typically cathodic in form and the diffusion current was considerably greater than in the presence of cyanide ion alone. However, these experiments demonstrate the lack of sufficient separation between the waves even under favourable conditions and the necessity for removal of the excess cyanide is apparent. It was found, however, that when the above experiment was repeated in the presence of an excess of formaldehyde, whilst the wave from free cyanide could be removed completely, so also could the wave from the silver-cyanide complex. No waves whatsoever were obtained.

Attention was now given to the possibility of applying the second method previously mentioned and here again the silver complex with cyanide ion was used. Many metals form stable cyanide complexes, but a consideration of the stability constants involved reveals that for general applicability of the method, particularly for the determination of silver in the presence of other heavy metals, nickel ion should serve best.

When increasing amounts of nickel solution were added to a $2 \times 10^{-4}M$ KCN solution, $10^{-1}M$ with respect to KNO_3, it was observed that the cyanide wave measured as described previously against the same reference electrode was progressively reduced till it eventually disappeared. Waves caused by excess nickel appeared at $E_{\frac{1}{2}}$ *ca.* —1·1V and by $Ni(CN)_4^{2-}$ at $E_{\frac{1}{2}}$ *ca.* —1·4V.

When nickel was added similarly to silver solutions containing an excess of cyanide ion, it was found that the silver-cyanide complex was not broken up and a true polarographic wave from the $Ag(CN)_2^-$ ion was obtained at $E_{\frac{1}{2}} = -0{\cdot}50V$ against the electrode previously described* *cf.* Fig. 1. A plot of $\log_{10}\frac{id - i}{i}$ against V gave an "n" value of 0·98, indicating a one electron transfer at the electrode.

The analytical utility of the wave was investigated and confirmed for silver concentrations within the range $10^{-4} - 10^{-6}M$. In some respects with $\leqslant 10^{-5}M$ solutions it was found more convenient for quantitative purposes to omit the Ni^{2+} solution and to correct the diffusion current for the small current observed with a cyanide "blank" solution at the same voltage. This was because the effect of adding nickel at the higher instrument sensitivities used for *ca.* $10^{-6}M$ Ag^+ solutions greatly increased the residual current.

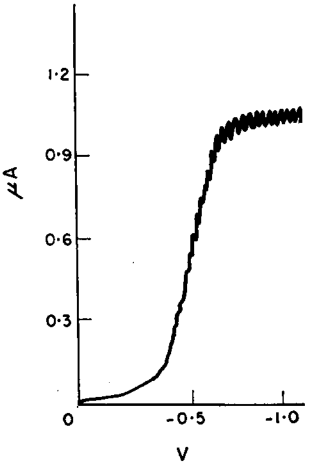


FIG. 1.—Polarogram of silver ions in the presence of excess KCN and $NiSO_4$.

Interferences. The interference of the following ions was determined: Co, Fe^{II}, Fe^{III}, Cu^{II} Ni, Zn, Cd, Pb, Tl^{I}, Bi, Th and Al. These tests were carried out with a two-fold excess of these ions on a solution $5 \times 10^{-5}M$ in silver ion, $2 \times 10^{-4}M$ in KCN, $10^{-1}M$ in KNO_3 and $10^{-5}\%$ with respect to methyl red, with and without added nickel sulphate as described above. The following did not interfere with the $Ag(CN)_2^-$ wave, but produced waves of the indicated $E_{\frac{1}{2}}$ values: Co (−1·4V), Zn (−1·35V), Cd (−0·9V) and Fe^{II} (−1·6V). By adjusting the pH of the solution to *ca.* 6·5 the following also did not interfere: Al (−2·0V), Bi (−0·15V) and Th (no wave).

Pb (−0·6V) and Tl^{I} (−0·5V) interfered by yielding waves at the same potentials as the silver complex. The interference of lead was overcome by addition of an excess of EDTA and careful buffering to pH 6·5–7·0. This moved the lead wave along to *ca.* −1·4V without affecting the silver wave. This method cannot, however, be applied for Tl because the latter does not form a stable EDTA complex. The interference of Tl^{I} could most probably be overcome by oxidation to Tl^{III}, but no further examination was made of this aspect.

Fe^{III} and Cu^{II} interfered by forming strong cyanide complexes and consuming

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* Measured against a dip-type calomel cell (E.I.L. Type RJ/23) immersed directly in the test solution, the value of $E_{\frac{1}{2}}$ was −0·26 to −0·28 V, S.C.E.

cyanide ion, but their interference was readily circumvented by adding a sufficient excess of cyanide ion to complex the silver and also the interfering ion, followed by an excess of nickel sulphate to remove the free cyanide. In this instance a complete polarogram in the cathodic area still reveals only the wave from $Ag(CN)_2^{2-}$, free Ni^{2+} and $Ni(CN)_4^{2-}$, since the cupricyanide complex originally formed quickly reverts to cuprocyanide *via* the reaction

$$2Cu(CN)_4^{2-} \rightleftharpoons 2Cu(CN)_3^{2-} + C_2N_2,$$

and the latter does not yield a polarographic wave in this medium. The same behaviour is observed with Fe^{III}, since ferricyanide is reduced at positive potentials with a dropping mercury cathode.

No extensive examination was made of the effect of anions, since the $Ag(CN)_2^-$ complex is much stronger than most other silver-anion complexes, but thiosulphate was selected as the most probable interference. However, under the recommended conditions no interference was observed from its reduction wave at −0·2V even when a ten-fold amount was present.

DISCUSSION

A procedure has been devised for the determination of silver based on the well defined reduction wave formed by its cyanide complex. The wave occurs at a potential at which very few other metal ions or their cyanide complexes are reduced, but procedures have been devised for the removal of interference by lead, copper and iron^{III}. Thallium^{I} is the only common cation still to interfere amongst those examined by us. Even strongly complexing anions such as thiosulphate do not interfere with the recommended procedure.

We have been unable to reproduce the wave previously reported by other workers for silver in a fluoride medium.[2] To the best of our knowledge the procedure recommended here is the only one that can be applied to obtain a completely defined polarogram for silver ion in dilute solution. Other procedures appear only to offer a diffusion current arising from the presence of silver ion in the solution.

EXPERIMENTAL

Apparatus

(a) Tinsley Mark 17 Recording Polarograph.

(b) Calomel Cell (Electronic Instruments Ltd. RJ/23) with $10^{-1}M$ KNO_3 electrolyte in place of saturated KCl solution. This was connected to the cell *via* a $10^{-1}M$ KNO_3 bridge.

Reagents

$10^{-3}M$ $AgNO_3$, $10^{-2}M$ KCN, $1M$ KNO_3, $10^{-2}M$ $NiSO_4 \cdot 8H_2O$, 0·01% methyl red, 20% ammonium acetate.

Procedure

Pipette ≤10-ml aliquots of $10^{-3}M$ $AgNO_3$ solution into 100-ml standard flasks together with 2 ml of $10^{-2}M$ KCN and 1 ml of $10^{-2}M$ Ni^{2+} solution. Add 10 ml of $1M$ KNO_3 as base electrolyte and 0·1 ml of 0·01% methyl red as maximum suppressor. Dilute to 100 ml with distilled water. Deoxygenate a sample of this solution in the polarographic cell by passing hydrogen through it for *ca.* 10 min, and obtain a polarogram over the range −0·3 to −0·8 V. (A drop time of 3 sec against a head of 35 cm of Hg was employed in this work at a sensitivity of 1·5 μA full scale deflection. The temperature was 18° and 2 units of damping were employed).

Silver in presence of Cu^{2+}

The following procedure may be applied for up to 0·6 mg of Cu^{2+} in the presence of ≤10 ml of $10^{-3}M$ Ag^+.

Proceed as described above, but add 7 ml of $10^{-2}M$ KCN followed by 2 ml of $5 \times 10^{-2}M$ Ni^{2+}, 10 ml of $1M$ KNO_3 and 0·1 ml of 0·01% methyl red. Proceed from this point as before.

Silver in presence of Pb^{2+}

The following procedure may be applied for up to 2 mg of Pb^{2+} in presence of $\leqslant$10 ml of $10^{-3}M$ Ag^+.

Follow the standard procedure, but after addition of the Ni^{2+} solution add 1 ml of $10^{-2}M$ EDTA and sufficient 20% ammonium acetate solution to restore the pH to 6·5–7·0, followed by 10 ml of $1M$ KNO_3 and methyl red. From this point follow the normal procedure.

Note: The two variations of the normal procedure should be capable of extension to deal with much larger amounts of Cu^{2+} and Pb^{2+} ions. The standard procedure may also be reproduced with aliquots of $10^{-4}M$ Ag^+ solutions which are subsequently diluted to 100 ml, using in this case $10^{-3}M$ KCN and $10^{-3}M$ $NiSO_4$, generally omitting the Ni^{2+} solution, and correcting for the small current from the cyanide ion, as measured on a separate solution not containing any silver ion. The nickel solution need only be added when dealing with interfering ions such as Cu^{2+} and Fe^{3+}.

Zusammenfassung—Eine wahre polarographische Welle für Silber in Cyanidelösung kann erhalten werden, wenn überschüssiges Cyanide mit Nickel abgebunden wird. Keines der gewöhnlichen Anionen stört, auch nicht Thiosulfat und von den Metallen, soweit untersucht, wurde nur Thallium(I) als störend gefunden. Die Koinzidenz der Bleiwelle kann durch zugabe von ÄDTE behoben werden.

Résumé—Une vague polarographique de l'argent peut être obtenue en milieu cyanure en éliminant l'excès de cyanure par addition d'un excès d'ions nickel. Les anions courants ne gênent pas, même les thiosulfates, et il en est de même des métaux étudiés, à l'exception de Tl^+. La vague due à Pb^{2+}, qui se superpose à celle de l'argent, peut être déplacée vers des potentiels plus négatifs par l'addition d'un excès d'acide éthylènediaminetétracétique.

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DETECTION AND ESTIMATION OF SOME POLYNUCLEAR HYDROCARBONS BY ELECTRON SPIN RESONANCE

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Summary—Certain polynuclear hydrocarbons are quantitatively converted into the free radical form on the surface of a strongly dehydrated silica-alumina catalyst. The resulting radical species are stable in the adsorbed state and their detection and estimation by electron spin resonance technique is described. Less than 10^{-10} mole of hydrocarbon can be detected. The application of this technique to the estimation of anthracene, perylene, dimethylanthracene and naphthacene is described.

INTRODUCTION

ALTHOUGH the high sensitivity of electron spin resonance technique makes it potentially attractive as an analytical tool, its application in analysis has so far been strictly limited. This is in contrast to the closely related phenomenon of nuclear magnetic resonance which has already demonstrated its importance in a wide field of analytical and structural applications.[1] The explanation for this difference lies partly in the unfamiliarity of microwave experimental technique and to a greater extent, so far as free radicals are concerned, in the short-lived nature of the species under investigation. The method is, of course, applicable only to elements or compounds possessing an unpaired electron or which can readily be converted into a free radical form. For species possessing an uncoupled electron-spin the theoretical limit of sensitivity approaches 10^9 radicals, while realisable sensitivities at room temperature with currently available commercial instruments approach 10^{11} uncoupled spins, or less than 10^{-12} mole.

Recently, Rooney and Pink[2] and Brouwer[3] have shown that certain polynuclear hydrocarbons are converted readily into a free radical form by electron transfer at the surface of a freshly activated silica-alumina catalyst. The apparently quantitative nature of the conversion with anthracene and the stability of the radical ions formed on the catalyst surface suggested that this novel reaction might have analytical implications. The present paper describes the application of the technique to the detection and estimation of a number of hydrocarbons.

EXPERIMENTAL

Apparatus

Electron spin resonance measurements: Electron spin resonance (ESR) spectra were obtained at room temperature with a conventional transmission spectrometer operating at 9370 Mc/sec and a magnetic field modulated at 100 kc/sec.[4] The instrument stability was such that at the amplifier gain settings used in analysis base-line drift amounted to less than 3% of full-scale deflection of the recorder over a period of several hr. Low-temperature dextrose-charcoal samples, with free radical concentrations in the range 10^{16}–10^{18} spins, were used as a check on amplifier gain and stability throughout the course of an analytical determination. The amplifier stability was such that the signal amplitude (peak to peak height on the first derivative curve) for the charcoal samples changed by less than 4% over a period of 3 hr after initial warm-up. The sensitivity of the spectrometer for hydrocarbon radicals was about 10^{14} uncoupled electron-spins, corresponding to $\sim 10^{-10}$ mole.

Sample tubes: Samples were contained in 6-mm glass tubes which were carefully selected to be of uniform bore and volume by direct comparison in the spectrometer using a benzene solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH) as standard. Tubes giving a signal amplitude which differed by more than 2% from the mean value were rejected.

The intensity of the signal from a given radical sample was found to be a function of the specimen depth in the microwave cavity. However, when the length of active sample lay within the range 19–22 mm the ESR signal intensity was unchanged. In all quantitative experiments the depth of sample was kept within this range.

Reagents

Catalyst: The silica-alumina catalyst was a commercial sample supplied by Imperial Chemical Industries Limited (Billingham Division) in pellet form (composition: Al_2O_3, 10%; Fe_2O_3, 0.05–0·10%; SiO_2, 89·7–89·9%). Its surface area measured by nitrogen adsorption was about 250 m^2/g. The pellets were crushed, sieved to 60 mesh B.S.S., and activated in air by heating to approximately 600° for a period of 2 hr. 44–60 mesh catalyst was chosen following a series of experiments in which this size of particle was found most convenient to handle in the analytical procedure described later. Activated catalyst was stored over phosphoric oxide in a desiccator. It gave no detectable ESR absorption. On exposure to the atmosphere it gradually lost activity through absorption of moisture. However, provided the catalyst was used in solutions well below its saturation capacity, brief exposure to the atmosphere was found to interfere in no way with the analytical results.

Solvents: AnalaR carbon disulphide and benzene were stored over active silica-alumina catalyst nd filtered before use. No further purification appeared necessary.

Polynuclear hydrocarbons: The anthracene used was Hopkin and Williams' micro-analytical standard. Perylene and naphthacene were obtained from Rütgerswerke-Aktiengesellschaft. 9,10-Dimethylanthracene was obtained from L. Light & Co.

Analytical procedure

At constant modulation depth and amplifier gain the signal amplitude (peak to peak height on the recorder trace) is directly proportional to the number of radicals present in the microwave cavity, provided the dielectric absorption of the samples remains the same and saturation effects are absent. For two samples of the same free radical species the signal amplitude is therefore directly proportional to the concentration. This relationship was found to hold for the DPPH radical in benzene solution over a ten-fold range of concentration. The radical concentration in an unknown solution may, therefore, be determined by direct comparison of the recorder trace for the unknown with that for a standard solution of the same radical.

No saturation effects were observed with the polynuclear hydrocarbons under the present experimental conditions when the microwave power was 35 mW. It should be noted that in the determination of relative concentrations by the method described a small degree of saturation can be tolerated, because with two solutions of the same free radical the signal amplitude will be reduced by approximately the same saturation factor.

The following procedure was adopted for the measurements on the polynuclear hydrocarbons. Differing amounts of the hydrocarbon solution were measured with an Agla micrometer syringe into separate sample tubes. Additional solvent was added to bring the level of solution in each tube to about the same height. Activated silica-alumina catalyst, previously placed in approximately the correct amount in small tightly-stoppered tubes, was now added slowly to the hydrocarbon solution using a small funnel, the contents of the tube stirred carefully for several min, and the tube stoppered. If it was found that the depth of active sample was under 19 mm, more catalyst was added and the contents of the tube again stirred carefully. Five or six ESR spectra with a sweep-duration time of 1 min were recorded for each catalyst-hydrocarbon system and the mean value for the signal amplitude was obtained. A series consisting of 30 determinations (*i.e.*, preparation of radical sample and measurement of ESR absorption) showed that the standard deviation of the value obtained for the ESR absorption from a single determination from the arithmetic mean for the series was about 5%. The time required for a complete estimation on a solution of unknown concentration, using two standards, is about 30 min.

The determination of absolute concentrations of radicals requires a comparison to be made with a stable free radical of different structure and the procedure is more complicated than that used for determining relative radical concentrations. The recorded spectrum, which is a first derivative, must be integrated to give the true absorption curve. The relative number of free radicals in the two samples is proportional to the areas under the respective absorption curves. Further integration gives, therefore, the ratio of the number of free radicals in the two systems. The accuracy of this procedure is limited largely by the errors in double integration, provided power-saturation effects are absent. A test of the procedure with perylene solutions is described later.

RESULTS

Anthracene

The spectrum obtained with anthracene adsorbed from carbon disulphide is shown in Fig. 1a. While the spectrum is less well resolved than that obtained with a solution of the hydrocarbon in 98 % sulphuric acid, the overall width and observed splittings leave no doubt that the paramagnetic species is the same as that in sulphuric acid and it is identified, therefore, as the radical cation $C_{14}H_{10}^{+}$ formed by electron transfer to a Lewis acid site on the silica-alumina surface.[2] The effect of anthracene concentration on the number of radicals formed is shown in Fig. 2. Over the range 0–20 μg a closely linear plot is obtained. At higher concentrations conversion into the radical form is incomplete. An unknown solution should therefore be diluted, if necessary after preliminary trial, so that the total hydrocarbon content falls within the stated range. The signal amplitude of the unknown solution may then be compared directly with one or more standard anthracene solutions in the same range.

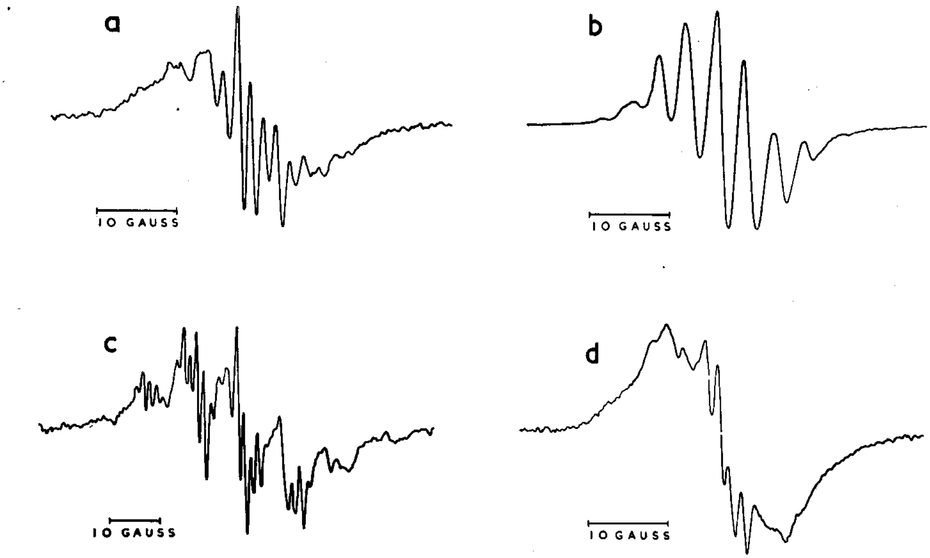

FIG. 1.—Electron spin resonance spectra (first derivative): (a) anthracene, (b) perylene, (c) 9,10-dimethylanthracene (adsorbed from carbon disulphide), and (d) naphthacene (adsorbed from benzene).

The stability of the anthracene radical is shown in Fig. 3. In the absence of detectable amounts of unconverted hydrocarbon in solution the radical decays slowly and measurement of the ESR spectrum may be made at any time within 20 min of preparation. In stronger solution decay is rapid. The process involved in the decay is not certain, but may be simple dimerisation involving reaction between a neutral molecule and the radical ion. It is significant that the resolution decreases as the signal decays indicating that new radical species are formed. Decay processes involving two radical-ions seem improbable in view of their charge.

Provided the catalyst-hydrocarbon system is covered with solvent there is no detectable interaction with oxygen and no precautions are necessary to protect the system from the atmosphere or moisture. In the absence of solvent the spectrum undergoes collision broadening with oxygen and no ESR absorption is observable.

This process is strictly reversible, the spectrum being restored when the oxygen is removed.[5] No detectable chemical interaction occurs between oxygen and the adsorbed radical ion in the absence of solvent even after periods up to 24 hr. Either carbon disulphide or benzene may be used as solvent. The colour of the radical in carbon disulphide and in benzene is blue.

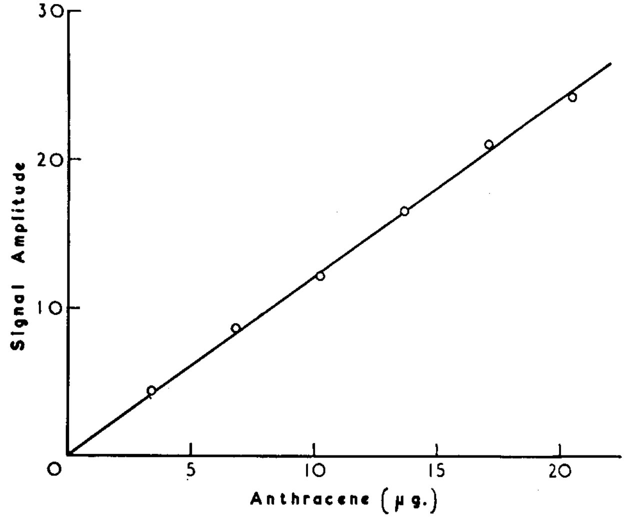

FIG. 2.—Signal amplitude (peak to peak height on the first derivative curve) as a function of concentration for anthracene in carbon disulphide.

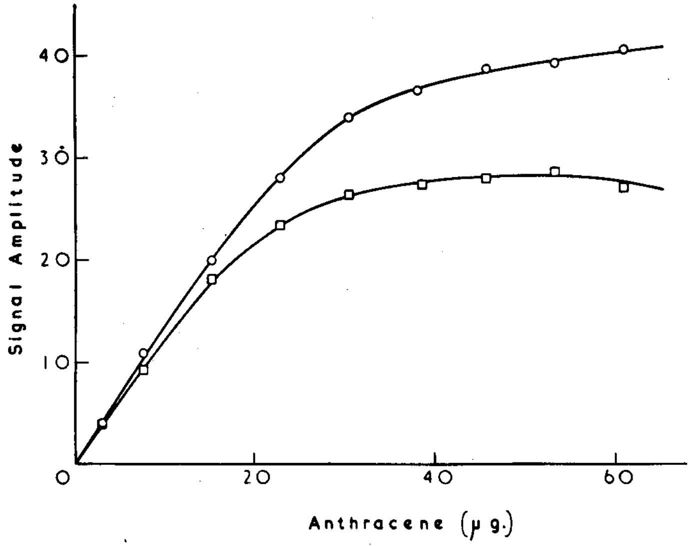

FIG. 3.—Signal amplitude as a function of concentration for anthracene in carbon disulphide. Measurements made within 15 min of radical formation (○) and 1·5 hr later (□).

Perylene

The perylene radical-ion spectrum is shown in Fig. 1b and the adsorption isotherm in Fig. 4. As in the case of anthracene a linear plot is obtained, the useful range being

0–140 μg. The quantitative nature of the conversion with perylene was checked by comparison of the spectrum obtained with a 7 × $10^{-4}M$ solution of perylene in carbon disulphide with that for a 3 × $10^{-3}M$ solution of DPPH in dry benzene employing in each case a sweep-duration time of 5 min. The results of a series of determinations, employing conventional techniques for the double integration procedure, are shown in Table I. Experiments 1–4 indicate that with the well-resolved and reproducible spectra obtained with high signal-to-noise ratio in these experiments, the error involved in this double integration procedure does not exceed ±3 %. In Experiments 5 and 6 different hydrocarbon and DPPH solutions were employed in the determination. The average error in the complete series of measurements does not exceed ±6 %. It may be noted that this procedure is not suitable for routine analysis because the time required for a single determination including the necessary double integration is a matter of hours. Electronic integration would clearly reduce the time involved to manageable levels, although direct comparison with a known hydrocarbon standard is preferable where one is available.

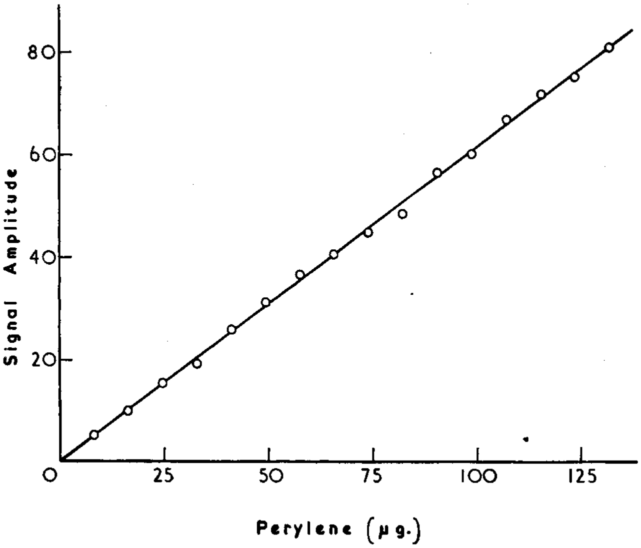

FIG. 4.—Signal amplitude as a function of concentration for perylene in carbon disulphide.

TABLE I.—FREE RADICAL CONCENTRATION IN 7·0 × $10^{-4}M$ PERYLENE SOLUTION ON ADDING ACTIVATED SILICA-ALUMINA CATALYST.

Experiment number	Free radical concentration, $M \times 10^4$
1	7·1
2	7·2
3	7·0
4	6·9
5	8·0
6	7·6

The stability of the perylene radical-ion is greater than that of the corresponding anthracene ion. Over a period of 24 hr the signal amplitude decreases by less than 5 %. Unconverted hydrocarbon in solution has no effect on the decay rate of the radical. The perylene radical-catalyst system has a deep violet colour which is detectable even at very low concentration.

9,10-*Dimethylanthracene*

The spectrum obtained with this hydrocarbon in carbon disulphide is shown in Fig. 1c and the relation between signal amplitude and solution concentration in Fig. 5, the useful range extending between 0 and 90 μg. In contrast to the results for anthracene and perylene the plot is slightly curved. To determine accurately the concentration of an unknown solution it would therefore be necessary to compare its signal amplitude with that of a standard dimethylanthracene solution not differing greatly from it in concentration; this may entail the preparation of two standard solutions. Because a solution of 9,10-dimethylanthracene is unstable in daylight, all operations involving the solution including the addition of the catalyst must be performed in a darkroom using a safelight only.

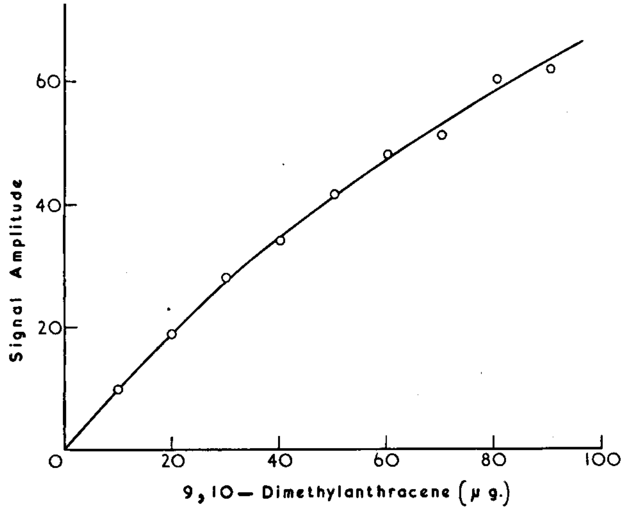

FIG. 5.—Signal amplitude as a function of concentration for 9,10-dimethylanthracene in carbon disulphide.

As in the case of anthracene the radical is fairly stable in the absence of detectable amounts of neutral hydrocarbon in solution and measurement of the ESR spectrum may be made at any time within 20 min of preparation. In strong solutions where unadsorbed hydrocarbon is present, the ESR signal decays rapidly in intensity and in resolution indicating that new radical species are formed. The dimethylanthracene radical-ion in carbon disulphide and in benzene is green.

Naphthacene

The ESR spectrum is shown in Fig. 1d and the signal amplitude-concentration plot in Fig. 6. The useful range extends between 0 and 200 μg; over this range the plot is slightly curved. Naphthacene in solution in carbon disulphide or benzene undergoes rapid photochemical oxidation in daylight and it was thought that the radical-ion in this case might be too unstable for analytical purposes. In fact the adsorbed radical has a remarkably high degree of stability, decaying less than 2% in 24 hr. Until the radicals are formed all operations must be carried out in the darkroom using a safe-light. The naphthacene radical-catalyst system has a bright green colour in benzene and in carbon disulphide.

DISCUSSION

The strong absorption in the ultraviolet and the intense fluorescence of many polynuclear hydrocarbons provide widely used analytical methods for their detection and estimation.[6] The electron spin resonance technique now described provides an alternative analytical method of high sensitivity and with an accuracy which compares favourably with other spectroscopic techniques at low concentrations. The method depends for its success on the quantitative nature of radical formation on a silica-alumina surface and on the stability of the resulting radical-ion species. The stabilising effect on free radical species of surface adsorption has been noted previously by Bijl, Kainer and Rose-Innes,[7] who reported marked stabilisation of semiquinone radicals adsorbed on alumina or silica gel. The observation that conversion into the radical form is complete within the limit of experimental error over a wide range of concentration for each of the hydrocarbons studied is of interest in view of the suggestion by Aalbersberg, Hoijtink, Mackor and Weijland[8] that two different species are formed by the reaction of aromatic hydrocarbons with strong Lewis acids, *viz.*, covalent complexes, in which there are no uncoupled electron-spins, and radical cations. Clearly the evidence does not support this contention for silica-alumina.

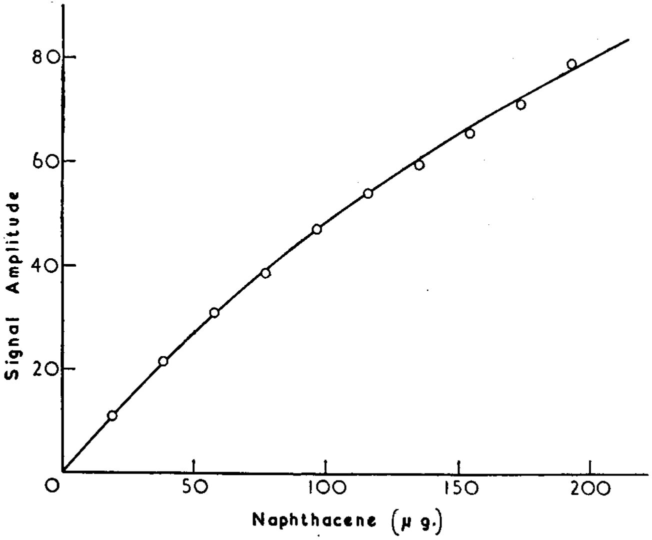

FIG. 6.—Signal amplitude as a function of concentration for naphthacene in benzene.

The useful concentration ranges for a particular catalyst sample in the technique now described depends entirely on its activity as an electron-acceptor. The catalyst used in these experiments was a commercial cracking catalyst readily obtainable in this country. More active catalysts have been described[9] for which the useful range would be greatly extended.

Because the g-factors of the hydrocarbon radicals all lie close to the free-spin value of 2·0023, considerable overlap of the spectra occurs with consequent mutual interference. Similar difficulties occur with fluorescence methods.[10] On the other hand, because benzene is inert to silica-alumina and because conversion into the radical form with naphthalene is negligible under the conditions of these experiments,[5] neither of these hydrocarbons interfere with the determination. In the case of naphthacene the electron spin resonance method has some advantage over conventional techniques. Solutions of this hydrocarbon in inert solvents undergo rapid photochemical oxidation in the light. When converted into the free radical form on the other hand naphthacene is surprisingly stable, only a marginal decrease in signal intensity being observed in 24 hr. This stabilisation in the free radical form is the more remarkable because the photochemical oxidation in solution may be assumed to involve excited species.

The application of this technique to the estimation of polynuclear hydrocarbons is limited to those which are converted readily into the free radical form. The ease with which this occurs on a silica-alumina surface varies widely and is a direct measure of the electron affinity of the hydrocarbon. This aspect is being further investigated and will be described elsewhere.

Acknowledgement—The authors thank Mr. R. K. Quigg for skilled assistance with the electronic instrumentation.

Zusammenfassung—Gewisse, vielkernige Kohlenwasserstoffe werden an der Oberfläche stark dehydrierter Silikat-Aluminiumoxyd-Katalysatoren quantitativ in freie Radikale verwandelt. Die Radikale sind beständig, solange sie an der Oberfläche des Katalysators adsorbiert sind und können mittels Elektronenspinresonanz bestimmt werden. Weniger als 10^{-10} Mole Kohlenwasserstoff kann bestimmt werden. Anwendung der Methode auf die Bestimmung von Anthrazen, Perylen, Dimethylanthrazen und Naphthazen wird beschrieben.

Résumé—Certains hydrocarbures polynucléaires sont transformés quantitativement en radicaux libres lorsqu'ils sont adsorbés à la surface d'un catalyseur constitué d'un mélange fortement deshydraté de silice et d'alumine. Les radicaux libres formés sont stables à l'état adsorbé et leur détection et leur dosage par résonance paramagnétique électronique sont décrits. Moins de 10^{-10} moles d'hydrocarbure peuvent être décelées. Le dosage quantitatif de l'anthracène, du pérylène, du diméthylanthracène et du naphtacène par cette technique est décrit.

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PRELIMINARY COMMUNICATIONS

Triethylenetetramine-N,N,N′,N″,N‴,N‴-hexa-acetic acid as a new titrimetric reagent

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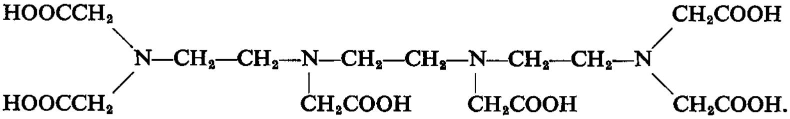
FROM the great number of polyaminocarboxylic acids which have been synthesised during the last two decades, the disodium acid of ethylenediaminetetra-acetic acid (EDTA) has been the most used as a titrimetric reagent. To a considerably smaller extent, and usually only in special cases, a few other acids have also been used, *e.g.*, 1,2-diaminocyclohexane-N,N,N′,N′-tetra-acetic acid (DCyTA), 1,2-diaminopropane-N,N,N′,N′-tetra-acetic acid (Methyl-EDTA, MEDTA), diethylenetriamine-N,N,N′,N″,N″-penta-acetic acid (DTPA), ethylene glycol-bis(β-aminoethyl ether)-N,N′-tetra-acetic acid (EGTA).

A most interesting substance has proved to be triethylenetetramine-N,N,N′,N″,N‴,N‴-hexa-acetic acid (TTHA), synthesised recently in the laboratories of Geigy Chemical Company (Basel, Switzerland)



This hexabasic acid offers for co-ordination bonding with metals four lone pairs of nitrogen electrons. Hence all requirements even for the formation of bimetallic complexes of the type Me_2X are fulfilled. Because of the supposed structure (formation of five and six-membering rings) it was possible to assume that the stability of the complexes formed would be very high and similar to the complexes with EDTA. This was confirmed by preliminary titrations with a solution of the disodium salt of TTHA at the same pH as in EDTA titrations, using the same very sensitive metallochromic indicators, *e.g.*, Xylenol Orange, Methylthymol Blue, Thymolftalexon, Fluorexon (Calcein), Eriochrome black T and Murexide.

EXPERIMENTAL

Reagents

0·05*M solution of the disodium salt of TTHA*: Prepared by dissolving 24·723 g of the acid (Geigy Chemical Company, Basel, Switzerland) in 130 ml of 1*M* sodium hydroxide solution in the warm, and diluting to 1 litre with redistilled water.

0·05*M solutions of metallic salts:* Prepared by dissolving the appropriate amounts of reagent grade chemicals (chloride, nitrate or sulphate) in redistilled water. The strengths of the solutions were checked complexometrically.

Indicators: 0·5% aqueous solutions of Xylenol Orange, Fluorexon(Calcein), Thymolftalexon and Eriochrome Black T as mixtures with potassium nitrate (1:100).

Other reagents included 1*M* nitric acid, 1*M* potassium hydroxide, concentrated aqueous ammonia, ammonia buffer, solid urotropine.

Titration of metals

The determination of single metals was carried out at similar pH values to those for EDTA titrations. In many cases two or even three methods of determination were chosen to ascertain the eventual influence on the formation of bimetallic complexes. The results are summarised in Table I.

TABLE I.—TITRATION OF VARIOUS METALS WITH TTHA

Metal	pH of the solution	Indicator	Back titration with	Composition of complex	Remarks
Bi	1–2	XO	Direct	1:1	
	3–4	XO	Th	1:1	
Th	3–4	XO	Direct	1:1	
Tl^{III}	3–3·5	XO	Direct	1:1	At 50–60°
	3–3·5	XO	Th	1:1	
	5–5·5	XO	Pb	1:1	
Zr	3–4	XO	Th	1:1	Slight displacement at the end-point, then indicator blocking
Ti	5–5·5	XO	Pb	2:1	As peroxocomplex
Ga	3–4	XO	Th	2:1	
	5–5·5	XO	Pb	2:1	
In	3–5	XO	Direct	1:1	In the hot
	5–5·5	XO	Pb	1:1	
	9·5	ERIO T	Direct	1:1	Sluggish end-point in the presence of tartaric acid
Sn^{II}	3–4	XO	Th	2:1	
Sn^{IV}	3–4	XO	Th	1:1	Slight displacement
Al	5–5·5	XO	Pb	2:1	After boiling with TTHA
Cr	5–5·5	XO	Pb	2:1	After boiling with TTHA. Displaced
	10–11	FRX	Ca	—	
La	5·5	XO	Direct	1:1	
Pb	5·5	XO	Direct	2:1	
Zn	5·5	XO	Direct	2:1	
	9–10	ERIO T	Direct	2:1	
Cd,Cu,Co,Ni	5·5	XO	Pb	2:1	
Co, Ni	10–12	THFX FRX	Ca	2:1	
Ni	10–11	MUR	Direct	2:1	
Hg	5·5	XO	Direct	2:1	
Mn	10–11	THFX	Direct	1:1	
	10–12	FRX	Ca	1:1	
Ca	10–12	THFX	Direct	1:1	
	10–12	FRX	Direct	1:1	
Mg	9	THFX	Direct	2:1	In TEA solution free of salts and in the presence of alcohol

XO = Xylenol Orange, THFX = Thymolftalexon, FRX = Fluorexon, ERIO T = Eriochrome Black T, MUR = Murexide, TEA = Triethanolamine.

DISCUSSION

Triethylenetetramine-N,N,N′,N″,N‴,N‴-hexa-acetic acid forms with the majority of bivalent elements bimetallic complexes of the type Me_2X^{2-}, with the exceptions of manganese and calcium which form 1:1 complexes in an alkaline medium. It seems that magnesium under limited conditions can form a 2:1 complex. Tervalent metals also form bimetallic complexes (probably Me_2X^0), excepting tervalent thallium, indium, bismuth and lanthanum, which form 1:1 complexes. Their existence, over a wide range of pH, has been proved by titrations in acidic and alkaline media. As expected, tervalent elements form 1:1 complexes. The only exception is titanium, which in the presence of hydrogen peroxide forms a 2:1 complex with TTHA. The existence of a similar zirconyl-peroxocomplex has not been proved with certainty. Among the more common elements, bi- and tervalent iron behave quite exceptionally. By back-titration with bismuth, thorium or lead, displacement of iron from the complex always took place and the function of the indicator failed.

Similarly, the TTHA complex of tervalent cobalt is formed slowly and non-quantitatively. Scandium likewise forms a 1:1 complex and is co-titrated with thorium. It is displaced quantitatively from its complex at pH 1–2 by bismuth. In slightly acidic solutions (pH 5) scandium reacts with Xylenol Orange even in the presence of excess TTHA.

From our experiments it appears that TTHA is at present the only compound of the complexan type forming sufficiently stable bimetallic complexes which can be used for titrimetric analysis. The different behaviour of bivalent and tervalent metals with TTHA can be applied for practical purposes. As an example the determination of a mixture of bismuth and lead is given.

Both of these elements form with EDTA only 1:1 complexes. Lead forms with TTHA a 2:1 complex, however, like other bivalent elements (see Table I). It is therefore possible to determine by two titrations, with EDTA and TTHA, the sum of both with great accuracy—theoretically regardless of their concentration ratios. Both titrations are carried out under the same acidity conditions with the same indicator. Results of these determinations together with the *Procedure* are given in Table II.

TABLE II.—DETERMINATION OF A MIXTURE OF BISMUTH AND LEAD WITH EDTA AND TTHA

Taken, *ml*		EDTA added, *ml*	Back titration with $Pb(NO_3)_2$, *ml*	TTHA added, *ml*	Back-titration with $Pb(NO_3)_2$, *ml*	Found, *ml*	
Bi	Pb					Bi	Pb
0·98	0·98	2·97	0·98	2·97	2·94	0·99	0·98
4·89	4·90	11·88	1·99	11·88	9·01	4·87	5·02
0·98	4·90	6·93	1·06	5·94	5·08	1·03	4·84
4·89	0·98	6·93	1·03	6·93	2·95	5·02	0·88
9·78	0·98	14·85	4·07	14·85	9·03	9·90	0·88
0·98	9·80	14·85	4·07	6·93	2·05	1·04	9·74
0·98	9·80	14·85	4·07	14·85	18·00	0·92	9·86
4·89	19·60	26·73	2·23	16·83	4·31	4·86	19·64
14·67	1·96	19·80	3·25	20·79	10·20	14·83	1·72

To the acid solution (0·05*M*) of bismuth and lead add an excess of 0·05*M* EDTA, adjust the pH to 5–5·5 with solid urotropine and titrate with 0·05*M* lead nitrate solution using Xylenol Orange as indicator. Carry out a second titration on a further aliquot of the mixture under the same conditions using 0·05*M* TTHA.

Table I shows further possibilities of such new determinations of mixtures of two elements which do not require screening reagents, *e.g.*, thorium-titanium, gallium-indium, tin^{II}–tin^{IV}, and generally, the combination of Me_1^{II}–Me_1^{III}, and finally, the determination of a tervalent element in the presence of a bivalent element and *vice versa*. From the analytical point of view special attention should be paid to the different behaviour of bivalent manganese (1:1 complex), magnesium (2:1) and calcium (1:1).

Theoretically very interesting are equilibria of the types:

$$Me_2X + 2Y \rightleftarrows 2MeY + X \qquad (1)$$

$$MeX + Y \rightleftarrows MeY + X \qquad (2)$$

where X and Y are the anions of the acids TTHA and EDTA (charges are omitted), respectively. The equilibrium is reached very quickly in the case of substitution labile complexes. The reaction shifts quantitatively to the right provided that the difference in stability of the complexes Me_2X and MeY is sufficient. In a substitution stable complex the reaction of Me_2X or MeX with Y proceeds, however, with an analytically immeasurable velocity. In such cases the cation Me is actually blocked or masked by the anion X. This phenomenon has also been observed with the complexes BiX, Al_2X and Ni_2X, while reaction (1) proceeds practically quantitatively for similar complexes with lead or tervalent iron.

It is possible to follow reaction (1) by titration with the solution of a salt of a metal which forms with both X and Y only 1:1 complexes. If reaction (1) proceeds quantitatively, 2Y are substituted for 1X and the titration consumption drops by one half. For orientation experiments 0·05*M* lanthanum nitrate solution has been used as a titrant with Xylenol Orange at pH 5–5·7 (urotropine). In this way it is possible to determine, for example, such binary mixtures as iron–aluminium, iron–nickel, nickel–lead, nickel–cadmium, nickel–zinc, *etc.*, because only the complexes Fe_2X, Pb_2X, Cd_2X, Zn_2X, *etc.*, react quantitatively according to equation (1).

Determination of iron and nickel

Procedure: In one aliquot determine the sum of the metals by back-titration of excess EDTA with lead nitrate solution using Xylenol Orange as indicator. To a second aliquot add a measured volume of TTHA and then EDTA. The excess of both is now titrated with lanthanum nitrate solution (Xylenol Orange). The TTHA is bound only to one metal (*e.g.* nickel), then EDTA to the other one (*e.g.* iron).

Calculation:

(a) 1 mole of iron or 1 mmole of nickel corresponds to 1 mmole of EDTA.
(b) 1 mole of nickel corresponds to 0·5 mmole of TTHA.
(c) 1 mmole of EDTA or TTHA corresponds to 1 mmole of lanthanum.

The second reaction can be followed by titration with a metal which forms with TTHA a 2:1 complex. If the reaction proceeds quantitatively, then consumption of titrant doubles, because Y replaces X which forms only Me_2X-complexes. For these titrations 0·05*M* lead nitrate solution and Xylenol Orange were used (pH 5·5-urotropine). In this way a mixture of iron and bismuth can be analysed because the BiX does not react with EDTA.

Determination of iron and bismuth

Procedure: In one aliquot determine the sum of iron plus bismuth complexometrically, *e.g.*, by back-titration of excess EDTA with bismuth nitrate solution at pH 1–2 with a Xylenol Orange end-point. To a second aliquot add a measured volume of TTHA and then EDTA. After adjusting the pH with urotropine, determine the excess of TTHA and EDTA with lead nitrate solution.

Calculation:

(a) 1 mmole of iron or bismuth corresponds to 1 mmole of EDTA.
(b) 1 mmole of bismuth corresponds to 1 mmole of TTHA.
(c) 1 mmole of lead corresponds to 0·5 mmole of TTHA (or 1 mmole of EDTA).

Determination of aluminium and iron

Procedure: To 5 ml of a 0·05*M* solution of aluminium and iron 10 ml of 0·05*M* TTHA were added and after boiling for 1–2 min and cooling, 12 ml of 0·05*M* EDTA were added. The solution was titrated with 14·5 ml of lanthanum nitrate solution to a Xylenol Orange end-point. As the sum of TTHA and EDTA (10 plus 12) corresponds to 22 ml of lanthanum solution, the sum is now Al_2X and FeY = 22 − 14·5 = 7·5 ml. The sum of AlY and FeY (titration with EDTA) corresponds to 10 ml. The difference of both titrations 10 − 7·5 multiplied by 2 (5 ml) gives the amount of aluminium. The difference 10 − 5 ml gives the amount of iron.

A number of other determinations of mixtures of two to three elements have been carried out, based on the above mentioned principles which do not require the use of masking reagents. Our further experiments with the combination of different new masking reagents are showing other unexpected possibilities of a highly selective determination of elements as well as the analysis of very complicated mixtures. Results of this further research will be published in due course.

Acknowledgement—The authors thank Dr. J. K. Aiken (Geigy Chemical Company, Manchester, England) for his initiation of this study and Dr. K. Krebser (Geigy Chemical Company, Basel, Switzerland) for his lasting interest and for providing the samples of triethylenetetraminehexa-acetic acid.

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Summary—The disodium salt of triethylenetetramine-N,N,N′,N″,N‴,N‴-hexa-acetic acid (TTHA) has been used for complexometric determination of a great number of metals and the existence of bimetallic complexes of most bivalent elements has been proved. Tervalent elements form bimetallic complexes too, except for bismuth, thallium, indium and lanthanum. By using EDTA and TTHA it is possible to determine some binary mixtures of elements without screening reagents. The new types of displacement reactions:

$$Me_2X + 2Y \rightleftharpoons 2MeY + X$$

$$MeX + Y \rightleftharpoons MeY + X$$

(X and Y are the anions of TTHA and EDTA) can be used for complexometric analysis. These possibilities are briefly discussed.

Zusammenfassung—Das Dinatriumsalz der Triäthylentetramin-hexaessigsäure (TTHE) wurde zur kompleximetrischen Bestimmung einer grossen Zahl von Metallen herangezogen. Tervalente Metalle formen bimetallische Komplexe, mit der Ausnahme von Bi, Th, In und La. Durch die Verwendung von TTHE in Verbindung mit ÄDTE ist es möglich Metallpaare ohne Maskierungmittel zu erfassen. Der neue Typ von Verdrängungsreaktionen:

$$Me_2X + 2Y \rightleftharpoons 2MeY + X$$

$$MeX + Y \rightleftharpoons MeY + X$$

(X und Y stehen für die Anionen von TTHE und ÄDTE) kann zur kompleximetrischen Bestimmung herangezogen werden. Diese Möglichkeiten werden kurz diskutiert.

Résumé—Le sel disodique de l'acide triéthylène tétramine héxacétique (TTHA) a été utilisé pour le dosage complexométrique d'un grand nombre de métaux. L'existence de complexes bimétalliques avec la plupart des éléments bivalents a été demontrée. Ces éléments trivalents forment également des complexes bimétalliques à l'exception du bismuth, du thallium, de l'indium et du lanthane. Grâce à l'emploi de l'E.D.T.A. et du T.T.H.A il est possible de doser des mélanges d'éléments sans avoir à utiliser des agents complexants. Les réactions du type:

$$Me_2X + 2Y \rightleftharpoons 2MeY + X$$

$$MeX + Y \rightleftharpoons MeY + X$$

(X et Y désignant les anions du T.T.H.A. et de l' E.D.T.A), peuvent être utilisés pour des dosages complexométriques. Les possibilités de la méthode sont brièvement discutées.

4-(2-Pyridylazo)resorcinol as a selective and sensitive spectrophotometric reagent for niobium^{V}

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WEHBER[1], and Sommer and Hniličková[2] examined 4-(2-pyridylazo)resorcinol (PAR) as a potential metallochromic reagent for several ions. The PAR molecule, in neutral or acid solution, exhibits a yellow colour, and reacts to form red chelates with a great number of ions including Pb, Zn, Cd, Cu, Ni, Co, Hg^{II}, U^{VI}, Pd^{II}, Y, La, In, Nd, Er, Zr and Ti. The colour reactions of many PAR complexes have been studied very fully by Pollard and his coworkers[3]. With the exception of those with uranium^{VI} and nickel, all these compounds are very readily broken down by ethylene diaminetetra-acetic acid (EDTA), and consequently PAR is an excellent metallochromic indicator for most of these ions.[4,5,6]

We have studied some of the reactions of this reagent with other metal ions, and find that it may be used as a very selective reagent for the spectrophotometric determination of trace amounts of niobium^{V} in a tartrate-buffered medium at pH 5·8. We have established by a variety of procedures that PAR reacts with niobium^{V} to form a moderately stable 1:1 red complex which absorbs strongly over a fairly broad and smooth absorption band (λ_{max} 5500 Å), and which, by our procedure, obeys the Lambert-Beer relationship over the range 0–70 μg Nb in a final volume of 100 ml. The effect of twenty-fold amounts of over thirty common cations and seven anions has been studied, and we have found that EDTA acts as a general masking agent. Tantalum forms only a very weakly coloured complex, and in the presence of sufficient tartrate up to a twenty-fold excess of this element (50 μg of Nb^{V} : 1000 μg of Ta^{V}) may be tolerated. Uranium and vanadium interfere by forming red complexes. Cyanide may be added to mask silver (which only forms a weak EDTA complex), and to break down the pink EDTA complex of cobalt^{II}. Cerium^{IV}, if present, should be reduced to cerium^{III} with ascorbic acid. None of the common anions interferes, and only phosphate, sulphide and sulphite cause difficulty. The order of addition of the various reagent solutions is important when certain foreign cations are present.

The colour reaction has been studied and the conditional stability constant of the PAR-Nb^{V} complex has been evaluated by two independent methods: the molecular extinction coefficient and the sensitivity index have also been measured. The colour system develops rapidly at room temperature, and is stable indefinitely once formed; the optimum pH range is not very critical. We have compared this new method for the spectrophotometric determination of niobium^{V} with the standard thiocyanate and 8-hydroxyquinoline procedures and find it to compare favourably in terms of ease of application, sensitivity, freedom from interference, range of application and stability. The method is now undergoing further examination in our laboratory, and independent examination by other workers. These, and other aspects of the procedure will be reported fully in the near future.

Meanwhile it may be noted that the reagent provides an elegant and sensitive spot test for niobium. The detection limit in a small test-tube or spot-plate is 0·1 μg, and the dilution limit is 1 part in 2,500,000. The colour reaction should be allowed to proceed for 1–2 min at room temperature, or the solution should be warmed (test-tube), whereupon the colour reaction is instantaneous.

The following ions do not interfere even when present in *ca.* twenty-fold excess: Pb, Bi, Cd, Hg^{II}, Fe^{III}, Fe^{II}, Al, Cr^{III}, Zn, Mn, Ca, Sr, Ba, Mg, Be, Sn^{II}, Sn^{IV}, As, Zr, Cu^{II}, Th, Ta, Ti, La, Ce^{III}, Mo, W, provided that sufficient amounts of EDTA and tartrate are present to maintain them in solution as their colourless or near-colourless complexes. If silver or cobalt is present, cyanide should be added to mask them. The EDTA must be added before the PAR and buffer, particularly when nickel is present, because this ion forms a complex with PAR which is not broken down by EDTA when this is added subsequently. Zirconium should be protected by EDTA before the buffer is added. It is the acetate ion of the buffer which is the effective masking agent for thorium.

SPOT TEST PROCEDURE

Reagents

10^{-3}M *PAR solution:* 0·2951 g of PAR, disodium salt, per litre of solution.

2×10^{-2}M *EDTA:* 7·445 g of disodium EDTA dihydrate in 1 litre of solution.

Buffer, pH 5·8: 150 g of sodium acetate trihydrate + 4·6 ml of glacial acetic acid in 1 litre of solution.

Procedure

To a drop of test solution containing $>0{\cdot}1$ μg of niobium in a sodium tartrate medium (*ca.* pH 5·8–6·4) in a small test-tube (or spot-plate) add 1 drop of EDTA followed by 1 drop of PAR and two drops of buffer. Warm gently on a hot water bath, or (spot-plate) allow to stand for 1–2 min. Carry out a blank test at the same time. The blank remains yellow, but the niobium-containing solution develops an orange to red colour depending on the amount of niobium present. The order of addition of reagents is important.

Acknowledgement—We wish to thank Dr. F. H. Pollard of the University of Bristol for providing us with a very pure sample of PAR.

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Summary—The reagent 4-(2-pyridylazo)resorcinol, PAR, in the presence of EDTA, gives a colour reaction with quinquevalent niobium which is not interfered with by any of the metals which normally accompany niobium. Of some 30 cations examined, only uranium$^{\mathrm{VI}}$ and vanadium$^{\mathrm{V}}$ interfere seriously. The reaction provides a sensitive method for the spectrophotometric determination of niobium, and is also applicable as a spot-test for amounts of niobium$^{\mathrm{V}}$ down to 0.1 μg. Even tantalum does not interfere when present in twenty-fold amounts, provided sufficient tartrate ion is added.

Zusammenfassung—4-(2-Pyridylazo)resorcinol (PAR) gibt in Gegenwart von ÄDTE mit fünfwertigem Niob eine Farbreaktion, die durch keines der mit Niob üblicherweise vorkommenden Metalle gestört wird. Von etw 30 untersuchten Kationen geben nur Uran(VI) und Vanadin(V) starke Störungen. Die Reaktion kann zu einer empfindlichen, spektrophotometrischen Bestimmung von Niob herangezogen werden und ist auch als Tüpfeltest bis herab zu 0.1 μg Nb verwendbar. Auch Tantal stört nicht, vorausgesetzt seine Menge überschreitet nicht das Zwanzigfache des Niob und genügend Weinsäure ist anwesend.

Résumé—Le 4 (2-pyridylazo) résorcinol, PAR, donne en présence d'E.D.T.A un composé coloré avec le niobium (V). Aucun des métaux qui accompagnent habituellement le niobium ne gêne. Parmi quelques 30 cations étudiés, seul l'uranium (VI) et le vanadium (V) gênent d'une façon notable. Cette réaction permet la mise au point d'une méthode sensible de dosage du niobium par spectrophotométrie; elle permet aussi de déceler le niobium (V) jusqu'à 0,1 μg. En présence de tartrate le tantale ne gêne pas même présent en quantités vingt fois supérieures.

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SHORT COMMUNICATIONS

Pyrohydrolytic determination of fluoride in milligram quantities of plutonium fluorides

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AMONG the methods available for the determination of the fluoride content of heavy metal fluorides two have found common use, *viz.* pyrohydrolysis[1,2,3,4,5,6] in a platinum, nickel or quartz apparatus, and distillation from sulphuric acid in a glass apparatus.[7,8] These methods, although straightforward when used on non-radioactive materials, present some experimental difficulties during the analysis of plutonium fluorides inside completely enclosed glove boxes. A modification of the pyrohydrolytic method was published by Powel and Menis[9] in which the heavy element fluoride is hydrolysed by heating in a current of moist oxygen. Because the use of a moist gas instead of steam has several advantages for work in glove boxes, *e.g.*, it avoids the condensation of steam on the panels and the use of a preheater assembly, the method has been tested on plutonium fluoride.

A sample of plutonium tetrafluoride was heated in a silica reactor tube at 800° in a current of moist air. The liberated hydrogen fluoride was absorbed in dilute sodium hydroxide solution, then determined using the zirconium-alizarin lake spectrophotometrically at 525 mμ.[10]

The precision of the method was determined by 12 analyses of a sample of plutonium tetrafluoride (obtained by the dry hydrofluorination of plutonium dioxide) which had been stored for several months. The mean fluoride content was found to be 22·8% (with a standard deviation of ±1%) compared with the theoretical value of 24·1%.

Because the mean fluoride content obtained from the precision analyses showed a significant bias from the theoretical, it was assumed that the fluoride content had decreased on long storage of the sample. Therefore, for ascertaining the accuracy of the method, a fresh sample of pure plutonium tetrafluoride was prepared and analysed six times. The results (Table I) indicate that the method gives a precision and accuracy of about 1%.

TABLE 1

Wt. of sample, *mg*	Wt. of oxide left behind, *mg*	Fluoride obtained, *μg*	Theoretical fluoride from wt. of oxide, *μg*	Fluoride in the sample, %
1·58	1·38	388	387	24·6
1·26	1·07	291	300	23·1
2·50	2·14	590	600	23·6
2·07	1·76	490	494	23·7
3·24	2·79	770	782	23·8
2·21	1·89	532	530	24·1
Mean	—	—	—	23·8
Theoretical	—	—	—	24·1

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Summary—The pyrohydrolytic determination of fluoride using moist air is described for the fluoride content of plutonium fluorides on the milligram scale.

Zusammenfassung—Die pyrohydrolytische Bestimmung in feuchter Luft wird für den Fluoridgehalt von Milligrammengen Plutoniumfluorides beschrieben.

Résumé—Les auteurs décrivent le dosage par pyrohydrolyse du fluor contenu dans les fluorures de plutonium à l'échelle due milligramme.

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Separation and determination of microgram or submicrogram quantities of gold in copper: Use of mercury as a collector

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INTRODUCTION

SEVERAL methods[1] have been reported for separating trace amounts of gold from aqueous solution. These include coprecipitation with tellurium, lead sulphide or a mixture of mercury and mercury amino salt,[2] extraction with ethyl ether, ethyl acetate[3] or dithizone,[4] *etc.* In the present paper, a new method of separation is proposed and applied to the determination of trace amounts of gold in copper metal. After dissolution of copper metal in nitric and hydrochloric acids, the solution is made ammoniacal. A small amount of mercury is added and the solution is stirred with a magnetic stirrer. Gold is collected into mercury globules as a dilute amalgam, leaving copper in the solution. The amalgam thus obtained is then separated, heated at 350° in a stream of nitrogen to remove mercury, and gold in the residue is determined by the photometric *p*-dimethylaminobenzylidenerhodanine method.[3,5]

EXPERIMENTAL

Apparatus

Hirama model II photoelectric filter photometer with 1-cm cells (0·5–6 μg of gold).
Hirama micro photoelectric filter photometer with 2-cm cells (0·1–0·5 μg of gold).
Atomic and Riken well-type scintillation counters.

Reagents

Mercury: Purify by aeration, washing with dilute nitric acid, and finally vacuum distillation.

Standard gold solutions (5 μg *and* 0·4 μg *of gold per ml*): Dissolve pure gold foil in *aqua regia*, and dilute with 1*M* hydrochloric acid.

Gold-198 *solution:* Dissolve gold-198 in *aqua regia*, and dilute with 1*M* hydrochloric acid or standard gold solutions. Determine the gold concentration photometrically.

Standard silver solution (50 μg *of silver per ml*): Dissolve silver nitrate in 0·1*M* nitric acid.

4% (w/v) *Sodium chloride solution.*

1% *and* 0·5% (w/v) *Sodium fluoride solutions.*

Rhodanine solution: 0·003% *p*-dimethylaminobenzylidenerhodanine in absolute ethyl alcohol.

All of the reagents used were of reagent grade. Water purified by ion-exchange was used throughout the work.

Procedure

Separation of gold from copper and silver. Transfer a weighed sample (*a* g or less of copper metal) containing 0·1 to 6 μg of gold to a beaker of suitable capacity. Add a few ml of water and 4*a* ml of concentrated nitric acid, and heat to dissolve. Add 3*a* ml of concentrated hydrochloric acid, and continue heating for 10 min. Cool the solution, and add 20*a* ml of concentrated ammonia solution. Cool and dilute to 50*a* ml with water.

To this ammoniacal solution add a small amount of mercury (2 ml for 50 to 500 ml of the ammoniacal solution, 0·5 ml for 2·5 ml) and a stirring bar, cover the beaker, and stir the solution with a magnetic stirrer. Select the size and the rotating speed of the stirring bar so that numerous mercury globules (1 to 4 mm in diameter) may be formed. After the prescribed time (see *Results and Discussion*) stop stirring, discard the solution, and wash the mercury several times with water by decantation. Transfer the mercury to a 50-ml beaker, and remove moisture by blotting with a few pieces of filter paper. Transfer the mercury to a silica combustion boat, 90 by 20 mm and 10 mm deep, and evaporate the mercury at 350° in a stream of nitrogen, avoiding prolonged heating of the residue. Dissolve the residue in the boat in 2 drops of concentrated nitric acid and 1 drop of water with the aid of a glass rod, then add 3 drops of *aqua regia.*

If 0·5 to 6 μg of gold is present in the solution, transfer the latter to a 50-ml beaker, and rinse the boat with 2 drops of *aqua regia* and small portions of water to make the total volume in the beaker about 10 ml. Heat the solution for a few min, and cool to room temperature in the dark. Filter the solution through a small sintered-glass disk (No. 4), catching the filtrate in another 50-ml beaker, and wash with small portions of 0·01*M* hydrochloric acid.

If less than 0·5 μg of gold is present in the solution, transfer the latter to a 10-ml glass dish, and rinse the boat with 2 drops of *aqua regia* and small portions of water. Evaporate the solution to dryness on a water bath. Dissolve the residue in 4 drops of 1:1 *aqua regia*, and evaporate just to dryness on a water bath (70°). Dissolve the residue in 1 ml of 0·1*M* hydrochloric acid, heat on the water bath (70°) for 1 min, and cool to room temperature in the dark. Filter the solution through a small sintered-glass disk (No. 4), catching the filtrate in another 10-ml glass dish, and wash with eight portions of 0·1*M* hydrochloric acid of 0·5 ml each.

Photometric determination of 0·5 *to* 6 μ*g of gold.* Evaporate the solution containing gold to dryness on a water bath, dissolve the residue in 1 to 5 drops of *aqua regia* and 0·5 ml of water, and evaporate just to dryness on the water bath (70°). Moisten the residue with 1 drop of concentrated hydrochloric acid, and again evaporate just to dryness on the water bath (70°). Add 2·5 ml of 0·12*M* hydrochloric acid and 5·0 ml of sodium chloride solution, heat for 5 to 10 min on the water bath, cool to room temperature, and add 0·50 ml of 1% sodium fluoride solution. Swirl the solution gently and add 0·50 ml of rhodanine solution dropwise. Transfer the solution to a 10-ml volumetric flask, dilute to the mark with water, and mix the solution by inverting the flask two or three times. Do not shake vigorously. After 15 to 20 min, measure the extinction of the solution in a 1-cm cell at 562 mμ against water. Determine the gold concentration by reference to a calibration curve prepared with the standard gold solution.

Photometric determination of 0·1 *to* 0·5 μ*g of gold.* Evaporate the solution containing gold to dryness on a water bath, dissolve the residue in 2 drops of 1:1 aqua regia, and evaporate just to dryness on the water bath (70°). Moisten the residue with 1 drop of concentrated hydrochloric acid, and again evaporate just to dryness on the water bath (70°). Add 0·25 ml of 0·12*M* hydrochloric acid and 0·50 ml of sodium chloride solution, heat for 1 min on the water bath (70°), cool to room temperature, and add 0·10 ml of 0·5% sodium fluoride solution and 0·05 ml of rhodanine solution. Transfer the solution to a 1-ml volumetric flask, dilute to the mark with water, and mix the solution with the aid of a small polyethylene rod. After 15 to 20 min, measure the extinction of the solution in a 2-cm cell at 562 mμ against water. Determine the gold concentration by reference to a calibration curve prepared with the standard gold solution.

Tracer experiments

Radioactive gold was used in order to investigate the deposition rate and the over-all recovery of gold. A known amount of gold-198 solution was added to a copper solution, and the separation procedure described previously was carried out. Aliquots (1 or 2 ml) were taken from the ammoniacal solution during stirring with mercury and from the solution at completion of the entire separation step, and their activities were measured by means of a well-type scintillation counter.

RESULTS AND DISCUSSION

The deposition of gold into mercury globules from the ammoniacal solution was investigated as a function of time by the use of gold-198 as a tracer. Typical results are shown in Fig. 1. From these results, the following times were established for achieving essentially complete deposition of gold

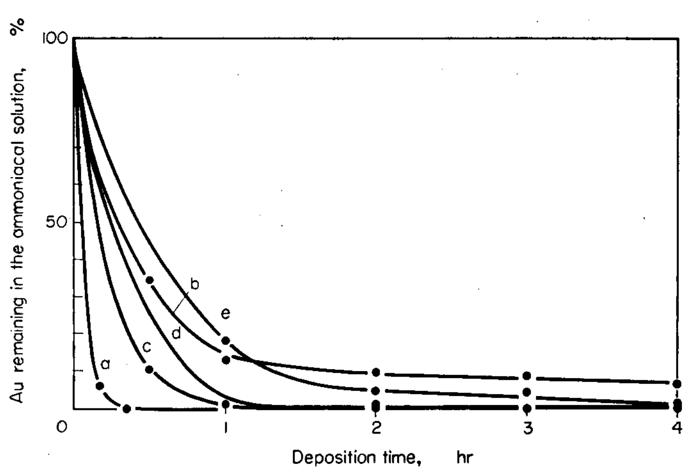

FIG. 1.—Deposition of gold into mercury globules from ammoniacal solution (mercury used: 2 ml):

(a) 50 ml of solution containing 5 µg of gold and 40 mg of copper,
(b) 50 ml of solution containing 5 µg of gold,
(c) 200 ml of solution containing 0·01 µg of gold and 40 µg of copper,
(d) 500 ml of solution containing 0·37 µg of gold, 60 µg of silver, and 10 g of copper,
(e) 500 ml of solution containing 0·24 µg of gold and 40 mg of copper.

from the solution containing copper; 1 hr for 50 ml or less of the ammoniacal solution, 2 hr for 200 ml, and 4 hr for 500 ml. However, if copper is absent from the solution, the deposition of gold is greatly retarded.

Synthetic solutions prepared from electrolytic copper (containing 0·013 ppm of gold and 6 ppm of silver), gold-198 and standard silver solutions, were analysed according to the procedure just given. The results shown in Table I indicate that gold in copper can be determined by this method within

TABLE I.—SEPARATION AND DETERMINATION OF GOLD IN SYNTHETIC SOLUTIONS

Exp. no.	Vol. of ammoniacal solution, *ml*	Present			Au found[a], *µg*	Au-198 recovered[b], %
		Cu, *g*	Ag, *µg*	Au, *µg*		
1	2·5	0·050	0	7·5	—	98
2	50	1·00	6	0·01	0·0	—
3	50	1·00	6	2·0	1·8	101
4	50	1·00	6	4·0	—	97
5	50	1·00	6	5·0	5·1	99
6	50	1·00	6	6·0	—	99
7	50	0·040	150	0·00	0·0	—
8	50	0·040	0	2·0	1·8	99
9	50	0·040	150	2·0	2·0	98
10	50	0·040	150	4·0	3·8	98
11	50	0·000	0	2·0	1·4	76
12	200	4·00	24	0·05	0·0	—
13	200	4·00	24	0·06	—	98
14	200	4·00	24	2·0	1·8	100
15	200	4·00	24	4·0	4·0	102
16	200	0·040	0	0·01	—	99
17	500	10·0	60	0·37	—	98
18	500	0·040	0	0·01	—	100

[a] By photometric procedure for 0·5 to 6 µg of gold.
[b] By radioactivity measurement (error, less than 2%).

an accuracy of 5% in the range of 1 to 100 ppm, and 10% at about 0·5 ppm. Less than 0·04 ppm of gold in copper can also be separated perfectly. Exp. 11 shows that the absence of copper from the ammoniacal solution results in an imperfect recovery of gold, in agreement with the results shown in Fig. 1. Therefore, a blank through the entire procedure was carried out after addition of a small amount (say 40 mg) of electrolytic copper to the solution. The blank value thus obtained corresponded to less than 0·01 μg of gold.

The calibration curve (concentration–extinction curve) in the photometric determination of gold is linear up to at least 0·6 ppm. The error is about 0·02 ppm in this range. No interference results from the presence of 100 ppm each of copper, iron and mercury; 5 ppm each of antimony, bismuth, cadmium, platinum and zinc; and 2 ppm of silver. However, even less than 0.5 ppm of palladium interferes with the determination of gold. In this experiment, all of the residues from the distillation of dilute amalgams had a weight of less than 0·5 mg, and no palladium was found in these residues by emission spectrographic analysis.

TABLE II.—DETERMINATION OF GOLD IN CRUDE AND ELECTROLYTIC COPPER

Sample	Sample taken	Vol. of ammoniacal solution, *ml*	Au found, *ppm*	
			Proposed method	Other methods
Crude copper I	36–54 mg	50	103, 96, 105, 105 (av.) 102	101[a]
	50 mg	2·5	100, 102, 98, 100 (av.) 100	95[b]
	3·2–4 mg	2·5	100, 102, 100 (av.) 101	95[c]
				(Ag 2762 ppm)
Crude copper II	48–72 mg	50	65, 68, 64 (av.) 66	64[a] 63[b] 69[c] (Ag 2269 ppm)
Crude copper III	160–220 mg	50	21, 22, 23 (av.) 22	22[a] 24[b] 23[c] (Ag 75 ppm)
Electrolytic copper	10 g	500	0·012, 0·013, 0·018[e], 0·010[f], (av.) 0·013	0·013[d] (Ag 6 ppm)

[a] Ion exchange-photometric method.
[b] Solvent extraction-photometric method.
[c] Dry assay.
[d] Ion exchange-neutron activation analysis.
[e] Sample analysed after addition of 0·10 μg of gold.
[f] Sample analysed after addition of 0·20 μg of gold.

The method was applied to the determination of gold in crude and electrolytic copper. The results are shown in Table II. In the case of crude copper, 3 to 5 g of the metal were dissolved in acids, and after settlement of small amounts of insoluble matter (silver chloride, silicates, *etc.*), an aliquot containing appropriate amounts of copper and gold was taken from the supernatant solution and analysed according to the procedure described previously. The results were in good agreement with those obtained by other methods of analysis.

Acknowledgement—The author wishes to thank Professor Shizo Hirano for his advice and encouragement.

A. MIZUIKE

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Japan

Summary—A new method of separation is described and applied to the determination of trace amounts of gold in copper metal. Gold is deposited into mercury globules from an ammoniacal solution of the copper. The resulting amalgam is heated to remove mercury, and gold in the residue is determined by the photometric *p*-dimethylaminobenzylidenerhodanine method. As little as 0.01 ppm of gold in copper can be separated and determined by the proposed method.

Zusammenfassung—Eine neue Trennungsmethode wird beschrieben, die am besten mit einer photometrischen Bestimmung von Goldspuren in Kupfermetall kombiniert wird. Gold wird aus ammoniakalischer Probelösung in Quecksilberkügelchen abgeschieden. Das Amalgam wird erhitzt und Gold im Rückstand mittels *p*-Dimethylaminobenzylidenrhodanin photometrisch bestimmt. Noch 0.01 ppm Gold können so abgetrennt und bestimmt werden.

Résumé—L'auteur décrit une nouvelle méthode de séparation et son application à la détermination spectrophotométrique des traces d'or dans le cuivre métallique. L'or est déposé dans des gouttelettes de mercure à partir de la solution ammoniacale de cuivre. L'amalgame ainsi formé est chauffé pour éliminer le mercure et l'or présent dans le résidu est dosé par spectrophotométrie en utilisant la p-diméthylaminobenzylidènerhodanine. Des quantités aussi faibles que 0,01 ppm d'or dans le cuivre peuvent être séparées et dosées par cette méthode.

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[1] E. B. Sandell, *Colorimetric Determination of Traces of Metals.* Interscience Publishers, Inc., New York, 3rd Ed., 1959. p. 494.

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Talanta, 1962, Vol. 9, pp. 953 to 954. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Organic Analysis (in Hungarian). L. MÁZOR. Müszaki Könyvkiadó, Budapest, 1961, 286 pp. 26.50 Hungarian forint.

THIS book fills a long-felt gap in the Hungarian technical literature in which no summarising work on organic analysis has so far been published. Conscious of this, the author has endeavoured to make his book useful both for scientific research and as a university manual. The work is planned to be published in three volumes, the first of which, issued recently, discusses methods of organic qualitative analysis. It deals with methods of preliminary testing and of qualitative elementary analysis. It also discusses the determination of physical constants, and considers the systematic qualitative analysis of organic compounds and their mixtures, as well as methods suitable for determining characteristic groups. It deals briefly with the application of ultraviolet and infrared spectrophotometry. Ways of compiling and utilising literature data are discussed and a method for producing derivatives is included.

The well-systematised, explicit text is completed by illustrative figures and tables. With the aid of these any reader possessed of elementary chemical knowledge, should find the best way for testing organic compounds.

ÉVA GÖRÖG

Quantitative Chemistry. A Laboratory Text. JURG WASER. W. A. Benjamin, Inc., Publishers, New York, U.S.A. Pp. 286. $3.25.

THE chief purpose of this book is to provide a laboratory text for a course in general and quantitative chemistry. A secondary objective is its use in any first course in quantitative chemistry.

Essentially, the text is a good quantitative analysis laboratory manual, featuring an expanded explanation of the principles and techniques used in each experiment. Many of these details are very worthwhile, but some of the explanations seem a bit too lengthy.

Twelve diverse type of experiments are described. These range from simple gravimetric chloride and acid-base titrations up through rather complicated coulometric analysis and the method of continuous variation. Most of the experiments are typical of those in a regular quantitative analysis course. However, several of the more advanced experiments could be classified as "instrumental methods". These should prove to be quite challenging for beginning students.

As a quantitative analysis laboratory text it is to be recommended. However, a great deal of the material seems beyond the capabilities of the usual freshman class. Its use at the freshman level should probably be restricted to talented groups.

F. H. FIRSCHING

Proceedings of the Second International Symposium on Enzymes in Clinical Chemistry (held at Ghent, Belgium in April, 1961). Butterworth, London, 1962. pp. 130. 60s.

THIS book, which appeared originally as numbers 3–4 of Pure and Applied Chemistry, Volume 3, comprises sixteen papers on a subject of rapidly growing importance and application. It would have been helpful if the reprint could have included English summaries to the French and German contributions; and the omission of the Symposium discussions is disappointing. Nevertheless, those concerned with the use of enzymatic techniques, whether in clinical medicine or biochemical research, will find much here to guide and stimulate.

There are a few papers dealing primarily with technique of assay but most are concerned with the measurement of enzyme concentrations in normal and pathological fluids and tissues as a guide to clinical diagnosis. In this respect, the papers describing studies of isoenzymes are of particular interest. As the work of F. Wroblewski indicates, it is obvious that such "diagnostic dissection" by use of starch-gel electrophoresis, *etc.* is going to find wide application in clinical laboratories. The author shows, for instance, that the isoenzyme pattern of plasma lactic dehydrogenase observed during the course of myocardial infarction provides a more reliable parameter of myocardial necrosis than does the measurement of *total* serum or plasma enzyme activity.

Other studies are concerned with the origin of tissue enzymes and the effect of activators, whilst one group has employed enzyme tests to measure the concentration of toxic intermediate metabolites in various diseases.

It seems probable that the price of this book will encourage readers to make use of the original publication of the Proceedings, which also has the advantage of a subject index.

D. R. STANWORTH

Talanta, 1962, Vol. 9, p. 955. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

UNITED KINGDOM

Wednesday 7 *November* 1962: **Fluoride, Teeth and the Analyst:** Dr. H. J. Cluley, Dr. J. Longwell and Dr. N. Jenkins: *Society for Analytical Chemistry.* The Wellcome Building, Euston Road, London, N.W.1.

Thursday 8 *November* 1962: **Solvent Extraction:** Dr. T. B. Pierce: *Society for Analytical Chemistry, Midlands Section.* Technical College, Nottingham.

Friday 9 *November* 1962: **Some Organic Applications of Polarography:** *Polarographic Society.* College of Advanced Technology, Loughborough.

Monday 12 *November* 1962: **Solvent Extraction of Inorganic Compounds. Some Recent Developments:** Professor H. M. N. H. Irving. *Society for Analytical Chemistry, North of England Section* and *Tees-side Section of the Royal Institute of Chemistry.* Constantine Technical College, Middlesbrough.

Tuesday 27 *November* 1962: **Recent Improvements in Separation Techniques:** Professor H. M. N. H. Irving and Dr. D. Gross. *Society for Analytical Chemistry, Physical Methods Group.* The Chemical Society, Burlington House, London, W.1.

Wednesday 5 *December* 1962: **Applications of X-Ray Fluorescence:** Mr. R. G. Stone, Mr. R. F. Sermin and Dr. E. T. Hall: *Society for Analytical Chemistry* with *Physical Methods Group.* The Chemical Society, Burlington House, London, W.1.

Saturday 8 *December* 1962: **Nuclear Magnetic Resonance:** Professor E. R. Andrew. *Society for Analytical Chemistry, North of England Section* and *Physical Methods Group.* Old Nag's Head Hotel, Lloyd Street, Manchester.

Friday 14 *December* 1962: **The Determination of Carbon and Hydrogen in Organic Materials:** Dr. A. M. G. MacDonald: *Society for Analytical Chemistry, Midlands Section* and *Microchemistry Group.* The University, Birmingham 15.

Wednesday 10 *July—Wednesday* 17 *July* 1963: **XIXth International Congress of Pure and Applied Chemistry:** London. The Congress will be organised into divisions for Organic, Inorganic, Analytical and Applied Chemistry. The Analytical Chemistry division will include the following sections:

1—*Trace Analysis.*

2—*Separation Methods.*

3—*Electroanalysis.*

4—*Teaching of Analytical Chemistry.*

Copies of the second congress circular are now available, and may be obtained from the Honorary Secretary, XIXth International Congress of Pure and Applied Chemistry, 14 Belgrave Square, London, S.W.1. The final date for applications to read papers and for submission of abstracts for the Congress is *Monday* 21 *January* 1963.

Friday 9–*Thursday* 15 *August* 1963: **6th International Congress of Nutrition, Edinburgh, Scotland.** This will include a session on **Isotopes in Nutritional Investigations.** Further information may be obtained from Miss A. D. Watson, Hon, Organising Secretary, 6th International Congress of Nutrition, Clinical Chemistry Department, Royal Infirmary, Edinburgh, 3, Scotland.

UNITED STATES OF AMERICA

Monday 33–*Thursday* 7 *February* 1964: **International Conference on Materials:** American Society *for Testing and Materials* and *International Union of Testing and Research Laboratories for Materials and Structures:* Sheraton Hotel, Philadelphia, Pa. Emphasis will be laid on materials technology, on world standardisation, and on the use of nuclear physics in the testing of materials. Further information may be obtained from H. H. Hamilton, Public Relations, American Society for Testing and Materials, 1916 Race Street, Philadelphia 3, Pa.

Talanta, 1962, Vol. 9, p. 956. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Ion-exchange study of thiocyanatochloro complexes of rare earth elements: H. Hamaguchi, R. Kuroda and N. Onuma (27 *August* 1962).

The determination of small amounts of calcium in the presence of large amounts of alkali metal salts by amperometric chelatometry: M. L. Richardson (28 *August* 1962).

Extraction of the cupferron complex of niobium: James F. Reed (30 *August* 1962).

Nephelometric examination of barium sulphate precipitation: A. G. Walton and T. Hlabse (5 *September* 1962).

Precipitation of metal 8-hydroxyquinolates from homogeneous solution—VI: Zinc: J. P. Jones, O. E. Hileman Jr., and L. Gordon (5 *September* 1962).

The determination of oxidising and reducing cations in transition-metal oxides using vanadium sulphate solutions: D. G. Wickham and E. R. Whipple (5 *September* 1962).

Coprecipitation with uranous oxalate: Jacob Block and Louis Gordon (5 *September* 1962).

Elimination of anionic interferences in the flame spectrophotometric determination of calcium: Use of glycerol as a releasing agent: T. C. Rains, H. E. Zittel and Marion Ferguson (7 *September* 1962).

Micro determination of the neutralisation equivalents of higher fatty acids by non-aqueous titrations: R. D. Tiwari and J. P. Sharma (10 *September* 1962).

Untersuchung der Kationensorption aus Komplexanmedium—IV: Trennung von Calcium und Magnesium aus Lösungen von Athylengly-kol-bis-(β aminoäthyläther)-N,N′-tetraessigsäure: Pavel Povondar and Rudolf Pribil (10 *September* 1962).

Contribution to the basic problems of complexometry—XII: Determination of aluminium in the presence of iron and titanium: Rudolf Přibil and Vladimir Veselý (10 *September* 1962).

The determination of microgram quantities of zirconium in iron, cobalt and nickel alloys by X-ray fluorescence: Owen H. Kriege and Joseph S. Rudolph (10 *September* 1962).

Comparison of solvents for the differentiating titration of phenols: N. T. Crabb and F. E. Critchfield (17 *September* 1962).

Determination of thorium in granite by gamma spectrometry and by radiotracer: S. A. Reynolds (17 *September* 1962).

A nomogram for acid-base titrations: E. Wanninen (17 *September* 1962).

Determination of gold-platinum-palladium-nickel and gold-palladium-rhodium-ruthenium in mixtures using ring colorimetry: E. J. Singh and Arun K. Dey (24 *September* 1962).

Arsenic in glass: J. A. Ryan and J. R. Sanderson (10 *September* 1962).

Estimation of the hydrogen content of palladium and palladium alloys from measurements of electrode potential and electrical resistance: J. C. Barton and F. A. Lewis (28 *September* 1962).

Isotopic dilution analysis by solvent extraction—V: Determination of traces of iron: Jiří Starý, Jaromír Růžička and Milan Salamon (28 *September* 1962).

The determination of traces of selenium and tellurium in samples of platinum by neutron-activation analysis: D. F. C. Morris and R. A. Killick (28 *September* 1962).

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