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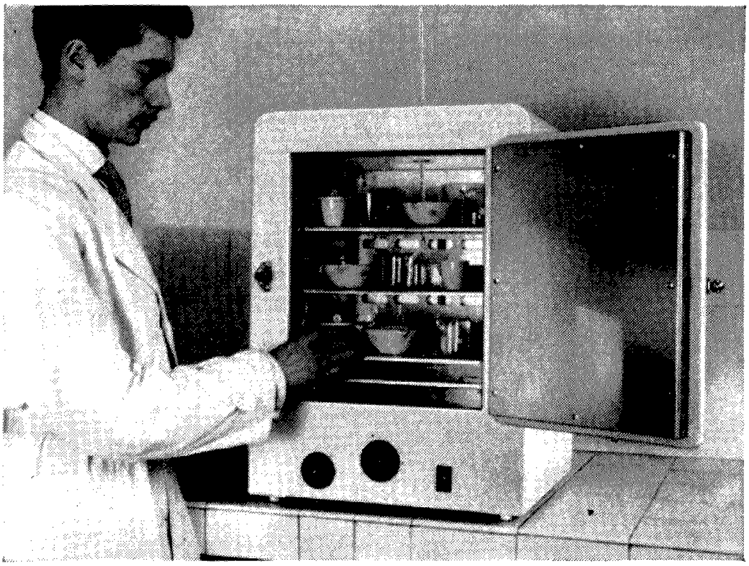

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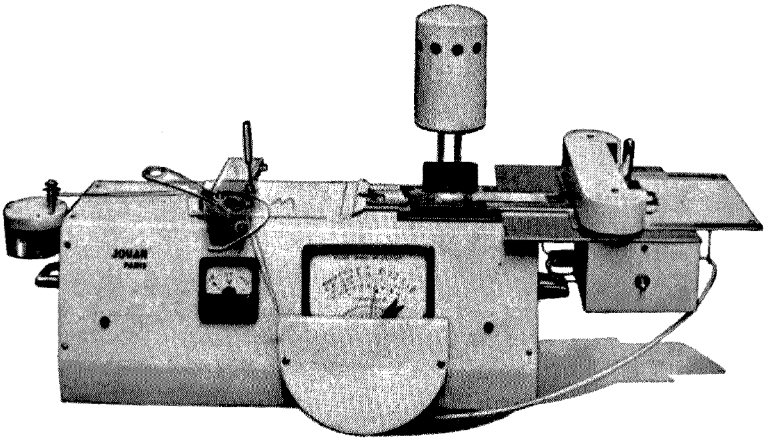

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# HIGH PRECISION TITRIMETRY*

## II. A SYSTEM OF WEIGHT TITRIMETRIC ANALYSIS USING ARBITRARY STANDARDS

E. BISHOP

*Chemistry Department, Washington Singer Laboraties, The University, Exeter, Devon (Great Britain)*

An examination of the mechanical precision of normal titrimetric operations[1], and comparison with practical precision has lent support to the idea that there exists a limiting precision, and therefore accuracy, for analytical processes beyond which improvement in mechanical precision gives no improvement in results. Further to establish this point, methods are suggested for increasing mechanical precision of measurement to the limit, and used to investigate precision and accuracy of certain determinations at a degree of mechanical precision beyond the inherent errors of chemical reaction and location of end-point.

Fully to realise the best precision of which ordinary volumetric methods are capable, it is necessary to recalibrate even standard glassware, since the limits of precision within which standards institutions rightly confine their certificates are rather wide. The reference standard is then a single weight, or, better, a set of weights, calibrated after the method of HERBO[2], to which the capacities of the vessels are related in the process of checking. To keep the cumulative errors small, extremely good balances are needed. All the many corrections must be applied during this process, and the finer the limits the more detailed the corrections must be. A balance capable of dealing faithfully with the weights will not cope with the larger flasks and pipettes, and vessels over 100 ml furthermore call for weights beyond the normal range. Really accurate large balances and weights are not common items of equipment.

Temperature and drainage corrections can be eliminated by weight titrimetry, but large balances and weights are still needed, and moisture adsorption errors are a disadvantage.

Since analytical chemistry is solely concerned with ratios: the ratio of one thing to another, a part to the whole (percentage composition) one concentration to another (titrimetric factors), etc., and not with absolute masses, standard units are merely a routine convenience and not a necessity, and arbitrary reference standards can be used. Thus in the calibration of volumetric glassware, the reference standard is a piece of metal, or a number of pieces of metal, which commonly approximate to an integral weight, but could be any other durable object. This principle can conveniently be applied to eliminate many of the errors and disadvantages of titrimetry.

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* Paper read at the Symposium on Analytical Chemistry held by the Midlands Society for Analytical Chemistry at Birmingham in August 1954.

## ARBITRARY STANDARD WEIGHT TITRIMETRIC ANALYSIS

The numerous corrections can be almost entirely eliminated by a technique of arbitrary standard weight titrimetry. This can be practised if a large balance is available, but requires no large weights. It uses a sealed flask full of liquid as the reference standard instead of a metal weight. Since the solution is in the same type, size and shape of vessel as the reference standard, vacuum corrections are virtually eliminated also (*vide infra*), temperature corrections are not needed, and, as the surfaces are closely similar, adsorption errors are minimised. This method of elimination of adsorption errors is commonly applied in atomic weight work and in micro-analysis.

### *Vacuum weighing correction*

When two solutions $S_1$ and $S_2$ are prepared by the method outlined below for inter titration, the flask plus solution in each case is poised against the reference standard, and therefore has in each case the same apparent weight in air as the standard.

Apparent weight of glass flask in air + apparent weight of $S_1$ in air
= Apparent weight of reference standard in air
= Apparent weight of glass flask + apparent weight of $S_2$ in air.

But the same flask is used in both cases, and its weight is constant.

$\therefore$ apparent weight of $S_1$ in air = apparent weight of $S_2$ in air.

If the true weights of the solutions are $W_{s1}$ and $W_{s2}$, their densities are $d_1$ and $d_2$ and the density of air is $d_a$, then

$$W_{s1} - W_{s1} \times d_1 \times d_a = W_{s2} - W_{s2} \times d_2 \times d_a$$

$$\therefore \frac{W_{s1}}{W_{s2}} = \frac{1 - d_2 \times d_a}{1 - d_1 \times d_a}$$

The error incurred by ignoring vacuum correction will be

$$\frac{1 - \dfrac{W_{s1}}{W_{s2}}}{1} = \frac{d_a(d_2 - d_1)}{1 - d_1 d_a} \approx d_a(d_2 - d_1)$$

Solution densities can be calculated with sufficient accuracy from the approximate volume of solution prepared. For example, in preparing approximately 0.05$M$ arsenic(III) and 0.01667$M$ bromate the densities are 1.00362 and 1.00164 respectively, and, assigning a value of 0.00123 for the density of air, the error incurred is 2.44 in $10^6$, or 0.00024%. Even with solutions very disparate in concentration and therefore density, the error is still very small, *e.g.* for aqueous dichromate, density 1.0025, and ferrous sulphate in 5$N$ sulphuric acid, density 1.10, the error is still only 9 in $10^6$, or 0.0009%.

When this correction is required, it can be calculated from the above equation.

## METHOD

### *Flasks*

Two vessels of suitable capacity are chosen as nearly alike as possible, preferably, though not necessarily, with long, narrow necks. Old volumetric flasks are convenient.

One should have a slightly longer neck and greater mass than the other to compensate for the glass removed in sealing. After cleaning, the heavier vessel is charged with a suitable amount of water and the neck smoothly sealed. This is the reference standard. For dealing with a wide range of non-aqueous solvents, the reference flask is charged with industrial spirit and chilled before sealing. A range of pairs of solution and reference flasks can readily be prepared, but they cannot readily be duplicated, so no units can be named.

### *Preparation of solutions*

The material is weighed out normally, dissolved in a suitable solvent, suitably treated, cooled, the solution quantitatively transferred to the empty flask and diluted on a rough balance till 1–10 g lighter than the standard. The two flasks are similarly wiped off with a slightly damp cloth and then with a dry one, and placed in the balance case for about 30 min to allow adsorption equilibration; complete uniformity of temperature is not required, merely sufficient similarity to avoid affecting the balance by convection currents. The flasks are placed on the pans, and water or solvent added to the solution carefully, finally with a hair capillary, until the solution flask is a few milligrams the heavier. The beam is fully released, allowed to swing, and the oscillations observed. Solvent evaporates from the solution flask at a rate which can be regulated by quite crude humidity control in the balance case, and when the

TABLE I

MECHANICAL PRECISION OF SOLUTION PREPARATION ON A SPECIALLY CONSTRUCTED STANTON 2 kg PRECISION BALANCE

| *Solution prepared* | *Weight of stoppered flask against counterpoise* | *Precision* % |
|---|---|---|
| 2 l hydrazine sulphate, aqueous | 16.3628 | 0.000 03 |
| | 16.3634 | |
| 2 l potassium bromate, aqueous | 16.3630 | |
| | 16.3632 | |
| 1 l borax, aqueous | 14.2866 | 0.000 02 |
| | 14.2866 | |
| 1 l potassium bromate, aqueous | 14.2868 | |
| | 14.2867 | |
| 1 l ammonium bromide, ethanolic | 15.6224 | 0.000 03 |
| | 15.6222 | |
| 1 l silver nitrate, methanolic | 15.6223 | |
| | 15.6225 | |
| ½ l ammonium bromide, methanolic | 6.5441 | 0.000 04 |
| | 6.5443 | |
| ½ l hydrochloric acid, aqueous | 10.4888 | 0.000 04 |
| | 10.4890 | |
| ¼ l potassium dichromate, aqueous | 3.5110 | 0.000 08 |
| | 3.5111 | |
| ¼ l potassium bromide, aqueous | 3.5110 | |
| | 3.5112 | |

rest point reaches the zero point, the flask is removed, stoppered, and the contents mixed.

In this way balance to ± 1 mg is readily attained, and with careful working under controlled humidity, ± 0.1 mg has been attained on a specially constructed Stanton 2 kg precision balance with 2-l flasks. The maximum attainable precision is therefore 0.000 005%, while even on a 100-ml flask 0.001% is readily achievable. The precision has been checked by weighing the stoppered flask against its reference counterpoise; some figures are given in Table I. With cruder balances, weighing by substitution is effective.

*Titrations*

Titrations may be made directly to visual indicator (better photoelectric) end-points, or to preset electrometric end-points. Or the dilution technique may be used, which affords a finer control of reagent addition. To maintain maximum precision, approximately 1 g of solution weighed to ± 10 µg is diluted to 1 l in a calibrated flask, and the burette read to ± 0.01 ml (equivalent to titrating to 0.000 01 g). For this dilution it is advisable to take the weight titration to within 0.025 g of the end-point, which is quite simple, and gives a 25-ml titration, with 25 ml after the end-point.

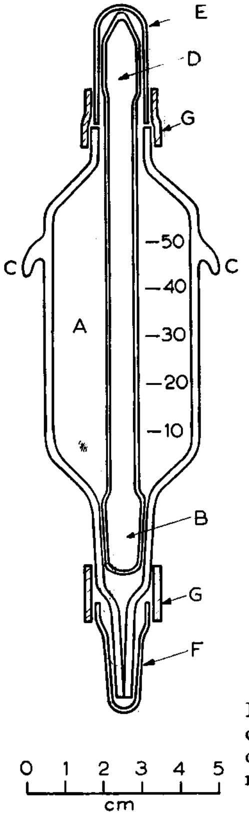

Fig. 1. Self-lubricating needle-valve weight burette. A. Burette bulb, capacity 60 ml; B. Ground in needle valve; C. Suspension hooks; D. Tubing of needle valve pinched flat at top to give finger grip; E. Glass cap: replaced by open tube for filling by suction: removed while manipulating valve; F. Glass jet cap; G. Thin rubber tubing.

*Weight burettes*

Most weight burettes are either clumsily heavy and have taps requiring lubrication[3,4], or are not susceptible to fine control[5,6]. The best answer appeared to be a tap lubricated by the solution, but totally enclosed to avoid loss. A needle-valve type of burette was developed as shown in Fig. 1. This calls for slightly different manipulation from an ordinary tap. A twist and push of the valve expels a quantity of solution, and very tiny drops can be ejected. It is filled by suction, or in the case of volatile solvents, under pressure. A pair are used, one the pipette, one the burette, in order to minimise adsorption errors. The two are charged and counterpoised, the

*References p. 412*

pipette emptied, rehung and the loss in weight determined, the burette used, rehung and the change again determined. Vacuum weighing corrections are still required, though if the solutions are closely equivalent, the error incurred in neglecting this correction is very small, *e.g.*, in a 50-ml bromate–arsenic(III) titration it is 2 in $10^6$.

TABLE II

MECHANICAL PRECISION OF OPERATIONS

| *Operation* | *Errors* | *Precision of complete single operation* |
|---|---|---|
| *a. At maximum attainable precision* | | |
| Weighing of sample | 10 g weighed to 3 $\mu$g (0.000 03%) | 0.000 06% |
| Preparation of solution | 2 kg weighed to 0.1 mg (0.000 005%) | 0.000 01% |
| Pipetting | 50 g weighed to 10 $\mu$g (0.000 02%) | 0.000 02% |
| Titration (i) direct | 50 g weighed to 10 $\mu$g (0.000 02%) | 0.000 02% |
| (ii) dilution | burette weighing, 50 g to 10 $\mu$g (0.000 02%)<br>dilution of 1 g weighed to 10 $\mu$g (0.001 × 0.02%)<br>to 1 l ± 0.03 ml (0.003 × 0.02%)<br>and burette read to 0.01 ml (0.001 × 0.02%) | 0.000 12% |
| Maximum theoretical precision per determination (i) direct | | 0.000 11% |
| (ii) dilution | | 0.000 21% |
| *b. At lower precision* | | |
| Weighing of sample | 10 g weighed to 0.01 mg (0.000 1%) | 0.000 1% |
| Preparation of solution | 100 g weighed to 1 mg (0.000 1%) | 0.001 % |
| Pipetting | 50 g weighed to 0.1 mg (0.000 2%) | 0.000 2% |
| Titration (i) direct | 50 g weighed to 0.1 mg (0.000 2%) | 0.000 2% |
| (ii) dilution | Dilution as above, burette read to 0.1 ml | 0.000 2% |
| | 10 g diluted to 1 l, burette read to 0.01 ml | 0.000 2% |
| | 10 g diluted to 1 l, burette read to 0.01 ml | 0.002 % |

TABLE III

NEUTRALISATION REACTION

Titration of borax by hydrochloric acid, approximately 0.5$N$, prepared from constant boiling acid at 753 mm, reduced to vacuum. Results expressed as percentage of HCl, calculated assuming borax to be formula pure $Na_2B_4O_7\cdot 10\ H_2O$.

| | *Direct titration to visual end-point* | *Dilution titration photoelectric end-point* | *Direct titration to buffer pH (glass)* | *Dilution titration with glass electrode* |
|---|---|---|---|---|
| | 20.2410 | 20.2382 | 20.2390 | 20.2374 |
| | 20.2362 | 20.2386 | 20.2372 | 20.2378 |
| | 20.2379 | 20.2378 | 20.2381 | 20.2377 |
| | 20.2344 | 20.2374 | 20.2368 | 20.2382 |
| | 20.2305 | 20.2379 | 20.2386 | 20.2378 |
| Scatter | 0.0105 | 0.0012 | 0.0028 | 0.0008 |
| Precision | 0.026% | 0.005% | 0.007% | 0.002% |
| Mean | 20.2360 | 20.2380 | 20.2379 | 20.2378 |

Uncertainty in the molecular weight of borax = 0.0055%.

### *The attainable precision*

With moderate care, the operations of solution preparation can be accomplished to ± 0.000 1%, of pipetting and titration to 0.000 05%, and weighing of the materials for preparing solutions to 0.000 2% on 5–10 g samples. Table II shows first the maximum mechanical precision of measurement attainable by these methods, and secondly some examples of operations at lower, readily achievable orders of precision. For weighings below 100 g, a specially adjusted and modified Stanton CB3 balance with a sensitivity of 3 $\mu$g at 100 g was used.

Thus, *e.g.*, preparation of 100 ml of solution to a precision of 1 mg, and dilution titration with a 100-fold dilution of this, gives a precision of 0.003%.

The mechanical errors can therefore be reduced to the order of 1 or 2 parts per million. This proves to be considerably smaller than the errors due to chemical and physico-chemical phenomena, the purity of materials, and the discrimination of end-point, so permitting the investigation of these factors without hindrance.

TABLE IV[a]

PRECIPITATION REACTION

Titration of potassium bromide (from potassium bromate) by silver nitrate, approximately 0.1*M*. Dilution titration, reference indicator electrode method[8], graphical potentiometric end-point.

| *Ratio Ag/O* | *Atomic weight of silver* | *Ratio KBr/Ag* | *Molecular weight of KBr* |
|---|---|---|---|
| 6.61744 | 107.8790 | 1.103217 | 119.0151 |
| 6.61758 | 107.8813 | 1.103170 | 119.0121 |
| 6.61751 | 107.8802 | 1.103201 | 119.0132 |
| 6.61738 | 107.8781 | 1.103162 | 119.0091 |
| 6.61731 | 107.8770 | 1.103191 | 119.0122 |
| 6.61770 | 107.8832 | 1.103179 | 119.0110 |
| 6.61760 | 107.8816 | 1.103229 | 119.0103 |
| Scatter | 0.0062 | | 0.0060 |
| Precision | 0.003% | | 0.003% |
| Mean | 107.8801 | | 119.0119 |
| International value | 107.880 | | 119.012 |

[a] Reproduced by kind permission of the Society for Analytical Chemistry, from the *Analyst*, 77 (1952) 679.

## RESULTS

Under the most favourable circumstances, and working under atomic weight conditions as exemplified in the work of HÖNIGSCHMIDT[7], the highest precision yet attained in a titrimetric process by the methods outlined is ± 0.001 5%. The accuracy is difficult to assess in this range, since the atomic weights concerned are not certainly known to greater accuracy, but may, in favourable circumstances, be said to reach 1 part per 100,000, or rougly one order less than the limiting mechanical precision of the measurements. Few determinations and methods of locating the end-point are capable of such precision, but certain selected and favourable reactions have been examined, and some results for each of three main types of titration are shown in Tables III to V.

## TABLE V

### REDOX REACTION

Titration of arsenious oxide by potassium bromate, approximately decinormal

| | *Direct titration to visual end-point* | *Dilution titration photoelectric end-point* | *Direct titration to predetermined potential* | *Dilution titration graphical potentiometric* |
|---|---|---|---|---|
| Ratio of $KBrO_3$ to $As_2O_3$ | 1.00644 | 1.00637 | 1.00635 | 1.00638 |
| | 1.00661 | 1.00642 | 1.00627 | 1.00641 |
| | 1.00626 | 1.00638 | 1.00634 | 1.00639 |
| | 1.00655 | 1.00643 | 1.00645 | 1.00640 |
| | 1.00640 | 1.00640 | 1.00638 | 1.00641 |
| Scatter | 0.00035 | 0.00006 | 0.00018 | 0.00003 |
| Precision | 0.018% | 0.003% | 0.009% | 0.0015% |
| Mean | 1.00645 | 1.00640 | 1.00636 | 1.00640 |
| Calculated ratio | 1.00641. Uncertainty in molecular weights 0.0058% | | | |

## CONCLUSION

With the aid of suitable balances and weights, mechanical errors of measurement can be reduced to a level at least one order below the chemical error. Very few titrimetric reactions, indicators or electrometric methods of locating end-points justify a precision of measurement greater than that of ordinary titrimetric analysis, and, even in the most favourable cases, there is a limitation upon the chemical degree of precision attainable, which is set by physico-chemical factors such as adsorption and reaction equilibria, and it would appear that there is an ultimate degree of precision and accuracy, around that of present day atomic weights, beyond which it is not possible to progress by normal chemical methods.

## ACKNOWLEDGEMENT

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## SUMMARY

A technique of arbitrary standard weight titrimetric analysis has been proposed for realising the ultimate degree of mechanical precision of which titrimetric processes are capable, and has been applied to reactions and methods of end-point location which are particularly favourable. A form of needle-valve weight burette is also described.

It has been found that, even in the most favourable cases and working under the conditions of atomic weight determination, there is a limit to the precision and therefore accuracy of the analytical results, which is set by physico-chemical considerations, and which is at least one order less than the maximum attainable mechanical precision of measurement.

## RÉSUMÉ

Une technique d'analyse titrimétrique employant un étalon arbitraire est proposée pour établir le degré de précision maximum des méthodes titrimétriques. On a trouvé que, même dans les cas les plus favorables, il existe pour les résultats analytiques une limite de précision déterminée par des considérations physico-chimiques et qui est inférieure à la précision mécanique des mesures.

*References p. 412*

## ZUSAMMENFASSUNG

Ein titrimetrisches Analyseverfahren mit einem willkürlichen Standardgewicht wurde zur Ermittlung der grösstmöglichen Genauigkeit titrimetrischer Methoden vorgeschlagen. Es hat sich herausgestellt, dass die Genauigkeit der analytischen Ergebnisse auf Grund physikalisch-chemischer Erwägungen begrenzt ist, und zwar liegt diese Grenze niedriger als die maximale mechanische Genauigkeit der Messungen.

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# THE SEPARATION OF BERYLLIUM FROM POLYVALENT CATIONS WITH A DIALLYL PHOSPHATE COMPLEXING RESIN

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## INTRODUCTION

In recent years a number of ion-exchange methods have been developed for separating beryllium from other polyvalent cations. In the earlier work[1,2] selective elution of the beryllium from other cations adsorbed on a sulphonated exchanger was conducted with solutions of inorganic acids or salts. However, it is evident that the relatively low resin affinity for beryllium, and its low selectivity (ratio of affinity for beryllium to affinity for other metals) renders such separations tedious if a number of different cations are present, and often requires a number of changes in eluting conditions before a separation is complete. More recently SCHUBERT *et al.*[3] have used sulphosalicylic acid (SSA) at pH 3.5–4.5 for the selective elution of beryllium from divalent cations, but as pointed out by these authors, trivalent cations such as aluminium are also eluted by SSA in this pH range. In a few instances, $Na_2EDTA$ which complexes only weakly with beryllium[4], has been used[5] or its use suggested[3] as a masking agent for other polyvalent cations and this allows the beryllium to be selectively adsorbed by the resin. Even in this instance it can be expected that the gain in selectivity is likely to be offset considerably by the combined effects of competitive adsorption by the unsequestered sodium ions and the slight sequestering action of $Na_2EDTA$ on the weakly adsorbed beryllium.

It has now been established that the complexing resin-sodium diallyl phosphate (NaDAP; $[(C_3H_5O)_2P(O)\,\bar{O}\,Na^+]_n$)[6] adsorbs beryllium in the presence of $Na_2EDTA$ to saturation capacity (*ca.* 4.9 mequiv./g of dry acid resin) irrespective of the aqueous phase beryllium concentration, while a large number of di- and trivalent cations are not adsorbed. The method thus allows the concentration of beryllium when the latter is only a minor or trace component in a mixture, and also the separation of the metal from minor contaminants.

## EXPERIMENTAL

### *Resins*

The NaDAP resin was prepared as previously described[6,7]. Its sodium–hydrogen exchange capacity was 4.93 mequiv./g dry $H^+$ form. The Zeo-Karb 225 (8–10% divinyl benzene) was obtained from Permutit Co. Ltd., London, and had a sodium–hydrogen exchange capacity of 4.68 mequiv./g of dry $H^+$ form. It was finally converted to the sodium form after a number of recycles between hydrochloric acid (0.5$N$) and sodium chloride (0.5$N$) solutions.

### *Analyses of beryllium*

Beryllium when present in solution in relatively large concentrations and in the absence of fluoride ion, was estimated gravimetrically as the oxide after precipitation with ammonia. When fluoride was present the solutions were diluted (× 80 to 100 depending on the beryllium concentration) and assayed colorimetrically using *p*-nitrobenzene–azo–orcinol reagent[8]. Fluoride or $Na_2EDTA$ do not interfere in these estimations, if present in low concentrations[9].

### *Adsorption and elution of beryllium*

A column of NaDAP resin (8 cm deep × 1 cm diam.) which had a total sodium-hydrogen exchange capacity of 4.19 mequiv. was constructed. A solution of beryllium nitrate containing 0.68 mg/ml beryllium and whose pH had been adjusted to 4.0 with ammonia was then passed through at a flow rate of 0.45 ml/min. Analyses of fractions of the effluent indicated the point of breakthrough, and passage of solution was continued until no more beryllium was adsorbed. The column was then washed with water and elution of the beryllium was effected with ammonium fluoride (20 ml, 0.5$M$).

The total beryllium eluted was 4.11 mequiv. No beryllium was detected in solutions obtained on wet oxidizing the resin with a mixture of sulphuric and nitric acids. Separate experiments also indicated that nitric acid (20 ml, 1.0$N$) elutes the beryllium quantitatively from a similar bed of resin. Solutions of $Na_2EDTA$ (2.5% w/v, 25 ml) or SSA (0.1$M$, 25 ml) at pH 4.0 failed to effect the elution of detectable beryllium ($\geqslant$1.0 mg) from the saturated resin. A similar experiment with a solution of beryllium (0.68 mg/ml) in the presence of $Na_2EDTA$ (2.5% w/v) gave a breakthrough curve co-incident with that obtained in its absence. Also the beryllium capacity of the resin was the same (4.12 mequiv.), when the beryllium concentration of the solution phase was reduced to 0.1 mg/ml. Breakthrough curves were similarly obtained for a column of Zeo-karb 225 in the sodium form and of equal sodium capacity (4.19 mequiv.) to that of the column of NaDAP in the previous experiments. The saturation capacities of the resin bed for beryllium in the absence and presence of $Na_2EDTA$ were 4.7 and 3.5 mequiv. respectively. Also elution with extra $Na_2EDTA$ (2.5% w/v, 20 ml) which contained no beryllium effected a complete removal of the adsorbed beryllium from the resins.

*Separation of beryllium from other cations*

A solution of $Na_2EDTA$ (2.5%, 100 ml) at pH 4.0 and containing 2.5 mg of each of the following cations. $Be^{+2}$, $Ca^{+2}$, $Sr^{+2}$, $Cu^{+2}$, $Zn^{+2}$, $Fe^{+3}$, $Al^{+3}$ and $La^{+3}$, was passed through a column of NaDAP (8 cm deep × 1 cm diam.) which had been previously washed with a solution of $Na_2EDTA$ (2.5% w/v, 20 ml). After passage the column was again washed with $Na_2EDTA$ solution (20 ml). Wet oxidation of the resin with sulphuric and nitric acids followed by analyses of the resulting solution showed that the beryllium was quantitatively adsorbed while no adsorption of the other cations took place. In separate experiments complete elution of the beryllium was effected with nitric acid (20 ml, 1.0*N*) or ammonium fluoride (20 ml, 0.5*M*). Analogous tests with solutions of $Cd^{+2}$, $Hg^{+2}$, $Pb^{+2}$ and $Mn^{+2}$ also showed that these cations are not adsorbed by NaDAP in the presence of $Na_2EDTA$.

## DISCUSSION

Breakthrough of beryllium occurs almost immediately with Zeo-karb 225 (a monofunctional sulphonated resin) if the solution contains $Na_2EDTA$. Without the latter breakthrough occurs after the passage of *ca.* 6½ bed volumes of solution and the total capacity of the resin for beryllium was 4.7 mequiv. that is 0.5 mequiv. in excess of its sodium capacity. This increase in capacity may be due to some of the beryllium existing in the resin phase as $BeOH^+$. In the case of NaDAP (a monofunctional phosphorylated resin) the breakthrough curve and capacity for beryllium is not influenced by $Na_2EDTA$. Although distribution coefficients ($K_d$) for beryllium between the NaDAP resin and aqueous phases containing $Na_2EDTA$ have not been measured, the absence of detectable beryllium from $Na_2EDTA$ solutions which have been passed through a beryllium saturated column suggests very high $K_d$ values. In conformity with the law of mass action $K_d$ should increase further to a constant maximum as the beryllium loading on the resin decreases. Also SSA which forms a stable complex with beryllium [$\log K^{\mathrm{M}}_{\mathrm{MHL}} \sim 4.9$][10] and which readily elutes it from Dowex-50 (a sulphonated resin)[3], fails to elute it from NaDAP. On the other hand $Na_2EDTA$ effects complete elution of the beryllium from Zeo-karb 225.

As the saturation capacity of NaDAP for beryllium is equal to that for sodium the adsorption mechanism is

$$Be^{+2} + 2NaDAP \rightleftharpoons Be(DAP)_2 + 2Na^+$$

The very high affinity of the NaDAP compared to sulphonated resins for beryllium also suggests that the latter is bound as a complex to the phosphate functional unit, but speculation on structure of complex would be premature at this stage.

As well as the polyvalent cations listed here from which beryllium was separated, it is also evident that it can be separated from bismuth and polonium(IV) under the same conditions[11,12]. Magnesium is not readily eluted with $Na_2EDTA$ from NaDAP, but it can be completely eluted with the disodium salt of cyclohexane-1,2-diaminetetraacetic acid which is a stronger sequestering agent[13]. As with $Na_2EDTA$, beryllium is not eluted with this reagent from NaDAP. Uranium(VI) ($UO_2^{+2}$) like beryllium is also quantitatively adsorbed by the resin in the presence of $Na_2EDTA$. Sodium carbonate however effects its quantitative elution, while the beryllium is retained on the resin bed, probably as an insoluble basic carbonate.

*References p. 415*

## SUMMARY

The complexing polymer sodium diallyl phosphate (NaDAP) when used in conjunction with disodium ethylene diamine tetraacetate ($Na_2EDTA$) separates beryllium quantitatively from alkaline earths (Ca and Sr), ferric and divalent cations of the first transitional period, aluminium and lanthanides, cadmium and mercury(II), bismuth and polonium(IV). The high affinity of NaDAP for beryllium should permit its concentration by several orders of magnitude, when present as a minor or trace component in a mixture of polyvalent cations. The results are compared with those obtained using sulphonated resin.

## RÉSUMÉ

L'allylphosphate de sodium polymère, en présence d'éthylènediaminetétracétate disodique, permet de séparer quantitativement le glucinium d'avec de nombreux autres cations. Les résultats sont comparés avec ceux obtenus à l'aide d'une résine sulfonée.

## ZUSAMMENFASSUNG

Polymeres Diallyl-natriumphosphat, in Gegenwart des Dinatriumsalzes der Äthylendiamintetraessigsäure ermöglicht eine quantitative Abtrennung des Berylliums von zahlreichen mehrwertigen Kationen. Die Ergebnisse werden mit denjenigen, die mit Hilfe eines sulfonierten Harzes erhalten wurden, verglichen.

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# SOLUBILITY PRODUCT RELATIONS IN THE RARE EARTH HYDROUS HYDROXIDES

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This paper is being presented to consider the solubility products of the rare earth hydroxides. A considerable amount of work has been directed to this topic[1]. The difference between "new" and "old" precipitated hydroxides has already been well established and seems to be a kinetic phenomenon in which a more soluble material undergoes ripening through dehydration and further crystalization to become more insoluble. However, there has been some question regarding the solubility product

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as effected by temperature. This paper deals with this point for the freshly precipitated hydroxides. An approximation is also offered to the thermodynamic heat of solution of these precipitates.

The study was carried out by dissolving a preweighed sample of ignited oxide in a slight excess of standard perchloric acid*. This solution was then titrated with increments of standard sodium hydroxide. Readings were taken after each increment of sodium hydroxide when the pH had come to equilibrium while the temperature was held within 0.2°. This was generally accomplished in about 2 min. In this manner a curve of the type shown in Fig. 1 was obtained by recording the pH as a function of the base added. In Fig. 1, point A represents the end-point of excess perchloric acid; B, the end-point corresponding to complete precipitation of the rare earth hydroxide; and C represents the point (B—A)/2. For varying temperature a family of curves was obtained, as shown in Fig. 2, with $T_1 > T_2 > T_3$. By use of the pH at C, the hydroxyl concentration was obtained. By use of the fact that the concentration of rare earth in solution at point C is one-half that at A, the solubility product was obtained by substitution in:

$$L_{\text{R.E.(OH)}_3} = (\text{R.E.})\ (\text{OH})^3$$

By use of the Van 't Hoff isochore and the assumption that $L_{\text{R.E.(OH)}_3}$ represents the equilibrium between solid and solution:

$$\text{Solid}_{\text{R.E.(OH)}_3} \rightleftharpoons \text{ionized solution}_{\text{R.E.(OH)}_3}$$

the heat of the solution was calculated.

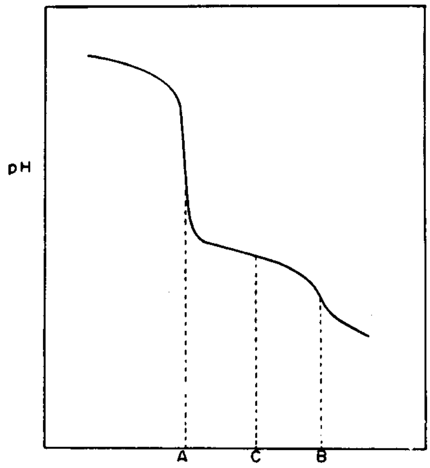

Fig. 1. Typical titration curve.

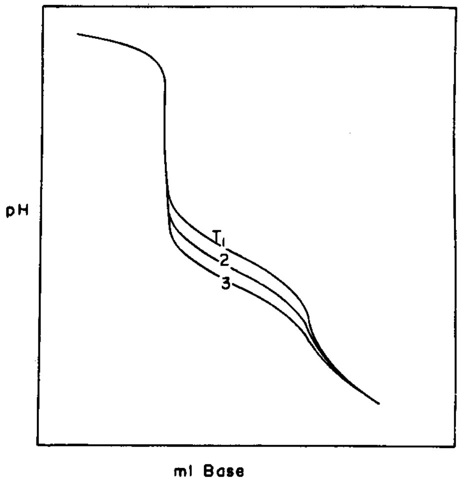

Fig. 2. Typical titration curve for variation in temperature.

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* Rational atomic weights are determined by this means as:

$$\text{At. Wt. R} = \frac{\dfrac{\text{Wt. R}_2\text{O}_3 \times 6000}{\text{mequiv. H}^+ \text{ equal to R}_2\text{O}_3} - 48}{2}$$

The data was obtained with a Beckman model H-2 pH meter. A Cenco Universal Relay Control and mercury contact thermostat regulated the temperature in a 10-gallon water bath. By this means the pH could be obtained to within 0.02 pH units and the temperature to within 0.2°. The rare earths had the following purities (with major impurities) as indicated by the manufacturers: La 99.9% (Ce, Pr), Pr 99.9% (Ce, Nd), Nd 99.0% (Pr, Sm), Sm 99.0% (Gd, Eu), Gd 98% (Sm, Nd, Dy), Y 99.0% (Dy, Gd).

TABLE I

SOLUBILITY PRODUCT DATA OF RARE EARTH HYDROXIDES

| *Rare earth* | *T°C* | *Rare earth at point C* | *pH at point C* | *Solubility product* |
|---|---|---|---|---|
| La | 10 | $5.48 \cdot 10^{-3}$ | 9.10 | $14 \cdot 10^{-18}$ |
| | 20 | $5.48 \cdot 10^{-3}$ | 8.68 | $0.64 \cdot 10^{-18}$ |
| | 30 | $5.48 \cdot 10^{-3}$ | 8.55 | $0.25 \cdot 10^{-18}$ |
| | 40 | $5.48 \cdot 10^{-3}$ | 8.10 | $11 \cdot 10^{-21}$ |
| Pr | 10 | $2.82 \cdot 10^{-2}$ | 8.23 | $14 \cdot 10^{-20}$ |
| | 20 | $2.82 \cdot 10^{-2}$ | 8.02 | $3.3 \cdot 10^{-20}$ |
| | 30 | $2.82 \cdot 10^{-2}$ | 7.77 | $5.8 \cdot 10^{-21}$ |
| | 40 | $2.82 \cdot 10^{-2}$ | 7.62 | $2.4 \cdot 10^{-21}$ |
| Nd | 10 | $3.72 \cdot 10^{-2}$ | 8.17 | $12 \cdot 10^{-20}$ |
| | 20 | $3.72 \cdot 10^{-2}$ | 7.90 | $1.9 \cdot 10^{-20}$ |
| | 30 | $3.72 \cdot 10^{-2}$ | 7.77 | $7.61 \cdot 10^{-21}$ |
| | 40 | $3.72 \cdot 10^{-2}$ | 7.65 | $3.24 \cdot 10^{-21}$ |
| Sm | 10 | $4.47 \cdot 10^{-2}$ | 7.82 | $1.3 \cdot 10^{-20}$ |
| | 20 | $4.47 \cdot 10^{-2}$ | 7.54 | $2.0 \cdot 10^{-21}$ |
| | 30 | $4.47 \cdot 10^{-2}$ | 7.32 | $39 \cdot 10^{-23}$ |
| | 40 | $4.47 \cdot 10^{-2}$ | 7.07 | $7.2 \cdot 10^{-23}$ |
| Gd | 10 | $1.21 \cdot 10^{-2}$ | 8.08 | $2.3 \cdot 10^{-20}$ |
| | 20 | $1.21 \cdot 10^{-2}$ | 7.86 | $0.46 \cdot 10^{-20}$ |
| | 30 | $1.21 \cdot 10^{-2}$ | 7.48 | $35 \cdot 10^{-23}$ |
| | 40 | $1.21 \cdot 10^{-2}$ | 7.25 | $6.8 \cdot 10^{-23}$ |
| Y | 10 | $3.75 \cdot 10^{-2}$ | 7.74 | $6.2 \cdot 10^{-21}$ |
| | 20 | $3.75 \cdot 10^{-2}$ | 7.65 | $3.3 \cdot 10^{-21}$ |
| | 30 | $3.75 \cdot 10^{-2}$ | 7.31 | $32 \cdot 10^{-23}$ |
| | 40 | $3.75 \cdot 10^{-2}$ | 7.10 | $7.3 \cdot 10^{-23}$ |

TABLE II

RELATIVE BASICITY OF RARE EARTH HYDROXIDES

| *Ratio* | *10°C* | *20°C* | *30°C* | *40°C* |
|---|---|---|---|---|
| La : Y | 2270 | 192 | 770 | 150 |
| Pr : Y | 22.8 | 9.95 | 18.2 | 33.2 |
| Nd : Y | 19.7 | 5.57 | 23.8 | 44.3 |
| Sm : Y | 2.12 | 0.59 | 1.23 | 0.98 |
| Gd : Y | 3.67 | 1.38 | 1.09 | 0.92 |
| Y : Y | 1.00 | 1.00 | 1.00 | 1.00 |

TABLE III

HEATS OF SOLUTION OF RARE EARTH HYDROXIDES

| *Rare earth* | *Temperature interval* | *ΔH°(kcal)* |
|---|---|---|
| La | 10–20 | 1.27 |
| | 20–30 | 0.42 |
| | 30–40 | 1.46 |
| Pr | 10–20 | 0.59 |
| | 20–30 | 0.75 |
| | 30–40 | 0.41 |
| Sm | 10–20 | 0.77 |
| | 20–30 | 0.72 |
| | 30–40 | 0.80 |
| Gd | 10–20 | 0.65 |
| | 20–30 | 1.13 |
| | 30–40 | 0.55 |
| Nd | 10–20 | 0.77 |
| | 20–30 | 0.44 |
| | 30–40 | 0.40 |
| Y | 10–20 | 0.25 |
| | 20–30 | 1.03 |
| | 30–40 | 0.69 |

Table I gives the major result of this work, giving vital data and calculated solubility product of the rare earth hydroxides. To be noted is the greater solubility for the greater atomic radii and lower temperature. It is fully recognized that these values do not represent equilibrium solubility data, but rather are to be associated only with the "new" hydroxide before it has had the opportunity to ripen. Table II shows the relative basicities as compared to yttrium hydroxide (comparison between like temperatures). This quite aptly characterizes the basicity which increases with increasing atomic radii and lower temperature. Table III shows the heat of solution for each hydroxide studied. It is estimated to be accurate to about 20%, considering temperature stability and accuracy in pH.

## SUMMARY

The solubility products for some rare earth hydroxides and their temperature dependence have been shown. Greater solubility is shown for larger atomic radii and for lower temperature.

## RÉSUMÉ

Les produits de solubilité de quelques hydroxydes de terres rares ont été déterminés.

## ZUSAMMENFASSUNG

Es wird über die Löslichkeitsprodukte der Hydroxyde einer Anzahl seltener Erden berichtet.

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# CHELOMETRIC TITRATION OF CALCIUM USING A MIXED INDICATOR*

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## INTRODUCTION

A problem often encountered in working with small amounts of clays is the determination of microgram quantities of calcium. The indicators now used for macrodeterminations are not suitable for determining very small quantities of calcium.

Recently Eriochrome Blue S.E.[1], Disodium salt of 3-(5-chloro-2-hydroxy-phenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid, used with a green screening dye (Naphthol Green B), was proposed as an indicator for the microtitration of calcium in deproteinized blood. The addition of the green dye greatly aids in the detection of the end-point.

This investigation reveals that this "mixed" indicator is suitable for the chelometric titration of calcium in clays and soils. Only manganese and strontium interfere with the end-point in the presence of potassium cyanide. Methyl alcohol aids in the detection of the end-point in semimicro titrations, but no improvement was observed for macrotitrations.

## EXPERIMENTAL

In preliminary investigations certain metals interfered with the titration and/or end-point. Therefore it was necessary to study the effect of methyl alcohol and potassium cyanide on the titration of calcium using the proposed indicator. Thus a known amount of calcium, methyl alcohol, and potassium cyanide were placed into 150-ml pyrex beakers singly and in combination to determine both the individual and combined effect of methyl alcohol and potassium cyanide. After placing these components into beakers, 2 ml of 10% potassium hydroxide was added to raise the pH above 12. Next the indicator, 6 drops of 0.1% Naphthol Green B in 25% methyl alcohol, and 6 drops of 0.1% Eriochrome Blue S.E. in 25% methyl alcohol, was added. The volume was adjusted to 30 ml and titrated with EDTA (disodium salt of ethylenediaminetetraacetic acid) until the color of the solution changed from a "dirty" red to blue.

Results from this first study led to the following semimicro chelometric titration: Place the solution containing the calcium into a pyrex beaker, add 15 ml of absolute methyl alcohol, 2 ml of 10% potassium hydroxide, 200 mg of potassium cyanide, and then add 6 drops each of 0.1% Naphthol Green B and Eriochrome Blue S.E. Titrate the solution with EDTA.

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** A portion of a thesis to be submitted by the senior author in partial fulfillment of the requirements for the Ph. D. degree.

The above procedure was used to study the effect of several ions on the end-point. The other ions were added prior to the addition of the methyl alcohol.

This method also was used to determine calcium in solutions in equilibrium with various calcium-clay samples. Centrifugation was used to remove the clay from the suspension and an aliquot of the solution was treated as described in the proposed method.

A final study was conducted to determine how the indicator, Calver II, used in the EDTA titration of macro-amounts of calcium[2], compared to this mixed indicator for the titration of exchangeable calcium from a soil sample. The test solution was prepared by leaching 10 g of soil with 200 ml of neutral normal ammonium acetate, evaporating to dryness, digesting the residue with nitric and perchloric acids[3], and making the solution to volume. The phosphorus was removed from a portion of this solution by passing it through an anion-exchange column (15 by 70 mm) and eluting with 30 ml deionized water. The column was filled with the nitrate form of Dowex-1 X8 (50 to 100 mesh). The sample plus the water washings were made to volume and an aliquot was used for the determination of calcium with each of the two indicators. The procedure followed was the same as with the semimicro titrations except that methyl alcohol was not used.

TABLE I

SEMIMICRO CHELOMETRIC TITRATION OF CALCIUM IN THE PRESENCE OF POTASSIUM CYANIDE AND METHYL ALCOHOL USING A MIXED INDICATOR

| *Treatment of solution* | *Calcium present (µg)* | *Calcium found[a] (µg)* |
|---|---|---|
| None | 10.0 | 10.0 |
| 200 mg KCN | 10.0 | 10.1 |
| 15 ml methanol | 10.0 | 10.3 |
| 200 mg KCN and 15 ml methanol | 10.0 | 10.0 |

[a] Mean of 3 titrations.

## RESULTS AND DISCUSSION

As shown in Table I, addition of potassium cyanide and methyl alcohol did not interfere with the titration of calcium using the proposed mixed indicator. In the presence of copper the apparent end-point is obtained without the addition of any EDTA unless the potassium cyanide is present. Thus it is necessary to add potassium cyanide prior to the addition of the indicator. Methyl alcohol made the change in color much more visible in the semimicro titrations, therefore it is recommended in the semimicro titrations of calcium using the mixed indicator.

The only ions studied which affected the end-point in the proposed method were manganese and strontium, Table II. Manganese decreased the amount of calcium found but strontium appeared to titrate as calcium. It is doubtful that in plants and soils amounts of manganese large enough to interfere will be found with very small amounts of calcium.

Three samples, of solutions in equilibrium with a clay, were titrated to determine the calcium present, and the precision of the method for this type of titration. The method was satisfactory as shown in Table III, with a good visible end-point.

The proposed mixed indicator compared satisfactorily with Calver II in calcium

### TABLE II

SEMIMICRO CHELOMETRIC TITRATION OF CALCIUM IN THE PRESENCE OF VARIOUS IONS USING A MIXED INDICATOR

| *Calcium present (μg)* | *Other ion present (μg)* | *Calcium found[a] (μg)* |
|---|---|---|
| 10.0 | 50.0 Magnesium | 10.4 |
| 20.0 | 50.0 | 20.3 |
| 30.0 | 50.0 | 30.6 |
| 10.0 | 50.0 Copper | 10.1 |
| 20.0 | 50.0 | 20.0 |
| 30.0 | 50.0 | 30.5 |
| 10.0 | 50.0 Zinc | 10.3 |
| 20.0 | 50.0 | 19.4 |
| 30.0 | 50.0 | 29.6 |
| 10.0 | 50.0 Phosphorus | 10.1 |
| 20.0 | 50.0 | 19.3 |
| 30.0 | 50.0 | 29.3 |
| 10.0 | 50.0 Iron | 10.3 |
| 20.0 | 50.0 | 19.3 |
| 30.0 | 50.0 | 29.7 |
| 10.0 | 50.0 Cobalt | 10.2 |
| 20.0 | 50.0 | 19.6 |
| 30.0 | 50.0 | 30.0 |
| 10.0 | 50.0 Aluminum | 10.2 |
| 20.0 | 50.0 | 19.8 |
| 30.0 | 50.0 | 29.5 |
| 10.0 | 50.0 Manganese | 9.4 |
| 20.0 | 50.0 | 17.7 |
| 30.0 | 50.0 | 25.6 |
| 10.0 | 30.0 Strontium | 23.3 |
| 20.0 | 30.0 | 33.1 |
| 30.0 | 30.0 | 42.4 |

[a] Mean of 3 titrations.

### TABLE III

SEMIMICRO CHELOMETRIC TITRATION OF CALCIUM IN EQUILIBRIUM SOLUTION OF CLAY SAMPLES USING A MIXED INDICATOR

| *Sample number* | *Calcium found (μg)* |
|---|---|
| 1. | 25.6 |
| | 25.1 |
| | 24.9 |
| | 25.3 |
| Mean | 25.2 |
| 2. | 29.8 |
| | 29.5 |
| | 30.1 |
| | 29.7 |
| Mean | 29.8 |
| 3. | 20.1 |
| | 20.3 |
| | 19.8 |
| | 20.3 |
| Mean | 20.1 |

recovered, Table IV, in the visibility of the end-point, and was superior in the stability of the indicator. Calver II fades rapidly after the completion of the titration but the mixed indicator maintained its color for 4 hours or longer.

Preliminary investigations reveal that the proposed indicator may be used in the chelometric titration of magnesium after calcium has been removed.

TABLE IV

COMPARISON OF MIXED INDICATOR WITH CALVER II FOR CHELOMETRIC TITRATION OF EXCHANGEABLE SOIL CALCIUM

| *Sample number* | *Calcium found[a] (mg)* *Calver II* | *Calcium found[a] (mg)* *Mixed indicator* |
|---|---|---|
| 1. | 0.56 | 0.59 |
| 2. | 0.56 | 0.59 |
| 3. | 0.56 | 0.58 |
| 4. | 0.61 | 0.59 |
| 5. | 0.59 | 0.58 |
| 6. | 0.60 | 0.58 |
| 7. | 0.59 | 0.59 |
| 8. | 0.60 | 0.61 |
| 9. | 0.60 | 0.58 |
| 10. | 0.59 | 0.59 |
| 11. | 0.58 | 0.57 |
| 12. | 0.57 | 0.57 |

[a] Mean of 2 titrations

## ACKNOWLEDGEMENTS

This study was supported in part by a grant from California Spray Chemical Corporation, Richmond, Calif. Experimental samples of Eriochrome Blue S.E. were supplied by Geigy Chemical Corporation, Ardsley, N.Y., and the Dowex-1 X8 was supplied by Dow Chemical Company, Midland, Mich. The cooperation of the above companies is gratefully acknowledged.

## SUMMARY

A mixed indicator for the chelometric titration of calcium has promise for the determination of microgram amounts of calcium in the presence of relatively high concentrations of other ions. Potassium cyanide eliminates the interference of certain metals. Addition of methyl alcohol improves the visibility of the end-point in a semimicro titration of calcium, although it does not improve the end-point for macro titrations.

This indicator also may be useful in the determination of magnesium after calcium has been removed from the sample.

## RÉSUMÉ

Un indicateur mixte est proposé pour le microdosage complexométrique du calcium, en présence de nombreux autres ions. Il peut être utilisé également pour le dosage du magnésium, en l'absence de calcium.

## ZUSAMMENFASSUNG

Zur Komplexometrischen Mikrobestimmung von Calcium in Gegenwart grösserer Mengen anderer Ionen wird ein Mischindikator vorgeschlagen, der auch zur Bestimmung von Magnesium in Abwesenheit von Calcium verwendet werden kann.

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# ULTRAVIOLET ABSORPTION SPECTRA OF α-NITROSO-β-NAPHTHOL AND ITS COPPER CHELATE

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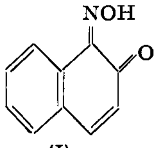
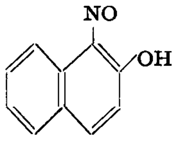
Although α-nitroso-β-naphthol was the first organic compound to be used for the analytical determination of a number of metal ions (especially Co) the structures of these metal complexes are not quite clear. The difficulty in assigning correct structures to these compounds lies in the fact that α-nitroso-β-naphthol itself may have two alternative structures (I) and (II) and no direct evidence is yet available to ascertain which one might represent the active form of this substance.



(I)



(II)

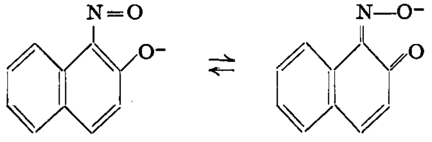
In the present work an attempt has been made to obtain some information in this respect from the measurement of the U.V. absorption spectra of α-nitroso-β-naphthol and its copper chelate. The same method was previously used by the author[1–3] for the determination of the nature of the bond between the metal atom and the organic ligand in the case of the chelates of acetyl acetone and quinoline-8-carboxylic acid.

Of the two possible structures of α-nitroso-β-naphthol (I) is quinonoid while (II) is benzenoid and these two forms should have completely different absorption spectra. The benzenoid form will have an absorption spectrum similar to naphthalene, in addition to some new bands due to localized transitions on the substituent and to charge migration between the π electrons on the ring and the substituent group. On the other hand the absorption spectrum of the quinonoid form will be rather broad and diffuse with no structure at all. The absorption band will be located below 300 mμ in the region where the absorption due to α-,β-unsaturated ketones appears. In addition there will invariably be an absorption band located at the longer wavelength side which may be associated with $n \rightarrow \pi^*$ transition having an intensity much less than the short-wave band.

It is evident from Fig. 1 that the absorption spectra of α-nitroso-β-naphthol in ethanol is more like that of a quinonoid compound than a benzenoid one, suggesting that structure (I) predominates in the benzenoid–quinonoid resonance of the system in ethanol. FEIGL[4] suggested that (I) is converted into (II) in acidic medium. In 0.1*N* ethanolic perchloric acid the spectrum of α-nitroso-β-naphthol is not affected at all (Fig. 2). In 0.1*N* ethanolic KOH, however, the spectrum is profoundly changed

*References p. 427*

(Fig. 2). The absorption spectrum in this medium closely resembles that of β-naphthol in alkaline medium (Fig. 3). In addition there is a weak absorption band at 425 mμ which may be associated with charge resonance between (III) and (IV).



(III) (IV)

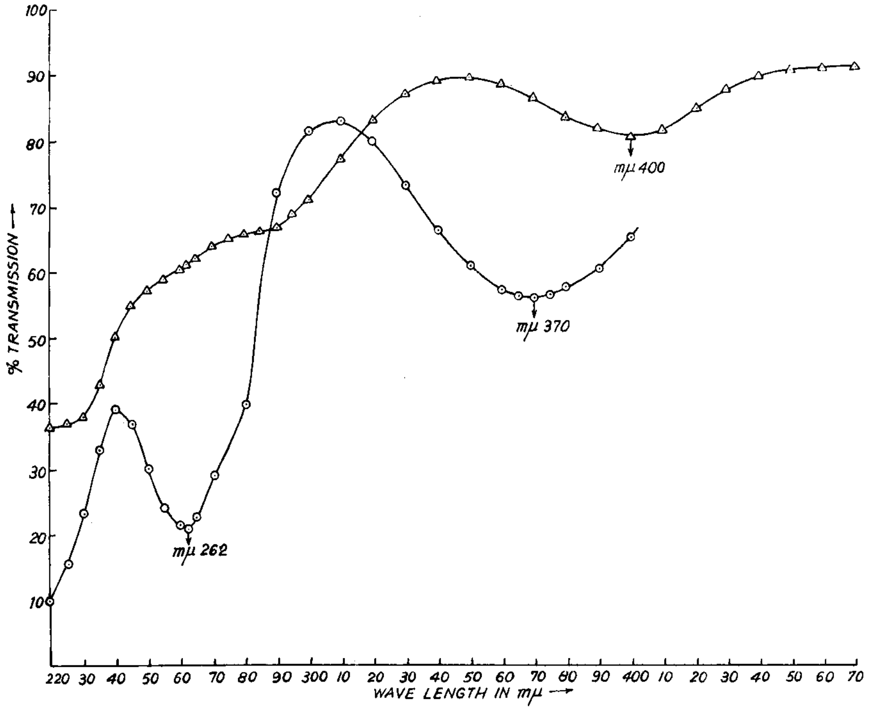
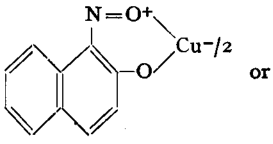


Fig. 1. U.V. absorption curves of α-nitroso-β-naphthol (o) and its Cu chelate (Δ), in ethanol.

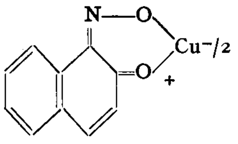
That the change in alkaline medium is not due to any permanent alteration in the structure of α-nitroso-β-naphthol is shown by the fact that when the alkali is neutralised the spectrum reverts to the original form in neutral ethanol.

The structure of the copper chelate is represented as



(V)

or



(VI)

In structure (VI), as the lone pair electrons of the oxygen undergo partial fixation, we expect the $n$ —$\pi^*$ band, *i.e.* the long-wave band of α-nitroso-β-naphthol, to shift towards the blue. In practice we notice (Fig. 1) a shift in the 370-mμ band towards the red to 400 mμ. The structure of the long-wave band is rather similar to the long-wave band of α-nitroso-β-naphthol in ethanolic KOH. This indicates that in the copper chelate the structures (V) and (VI) are present in almost equal amounts. The planarity of the molecule in the copper chelate will undoubtedly facilitate the charge resonance envisaged in (V) and (VI).

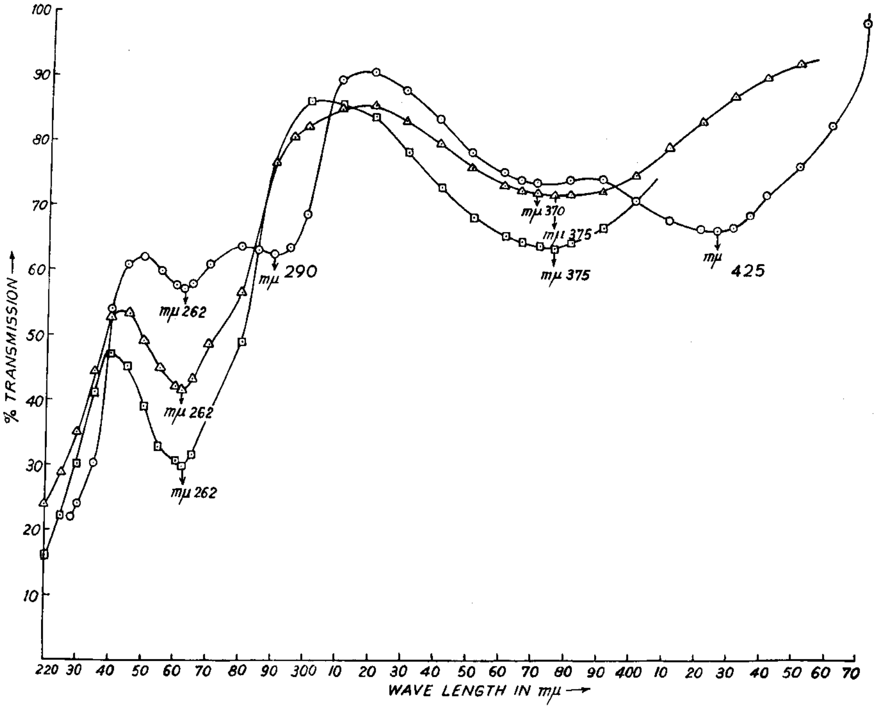


Fig. 2. U.V. absorption curves of α-nitroso-β-naphthol, (□) in 0.1$N$ ethanolic $HClO_4$, (o) in 0.1$N$ ethanolic KOH, (Δ) after neutralisation of the alkaline solution with 0.1$N$ ethanolic $HClO_4$.

Ultraviolet absorption measurements were carried out with the help of the Beckman model D.U. quartz spectrophotometer using a 1-cm quartz absorption cell. The ethanol used was refluxed for 6–8 h with solid caustic soda and then distilled. It showed complete transmission down to 220 mμ. Purification of α-nitroso-β-naphthol was carried out in the following way. 1 g of Schering-Kahlbaum's A.R. α-nitroso-β-naphthol was dissolved in 100 ml of spectroscopically pure ethanol and the solution was passed several times through fresh columns of E. Merck's Brockman alumina (8 cm × 0.5 cm). Each treatment was followed by spectrophotometric examination of the substance in solution till no variation in its U.V. absorption curve was noted.

A portion of the ethanolic solution was immediately employed for absorption measurement of the ligand in neutral, acidic, and alkaline media, while the other part was used in the preparation of the copper complex. (In the copper complex the percentage of the metal was found to be somewhat higher than the theoretical value. Such a discrepancy is, however, well known for the chelates of α-nitroso-β-naphthol, a reason why they have often been regarded as salt-type associated compounds. This assumption is ruled out by the fact that the absorption curve of the chelate shows no indication of unaffected ligand molecule, and as such the cause of the discrepancy in the analytical results should be looked for elsewhere.) E. Merck's β-naphthol was purified by recrystallising twice from spectroscopically pure ethanol. Solutions employed for absorption measurements were $10^{-4}$ –$10^{-5}M$.

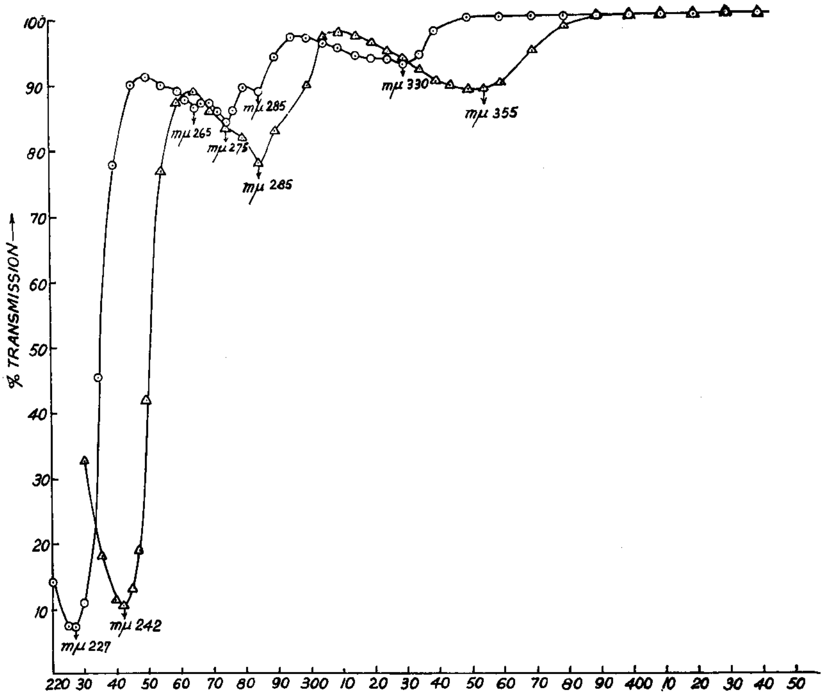


Fig. 3. U.V. absorption curves of β-naphthol in ethanol (○), and in 0.1N ethanolic KOH (△).

ACKNOWLEDGEMENT

The author's grateful thanks are due to Dr. SADHAN BASU, D.Sc., F.R.I.C., Reader in Physical Chemistry, University College of Science, Calcutta, for his keen interest and helpful suggestions in the course of the present work.

*References p. 427*

## SUMMARY

From a comparative study of the U.V. absorption spectra of α-nitroso-β-naphthol and of β-naphthol in neutral ethanol and in the presence of 0.1$N$ $HClO_4$ and 0.1$N$ KOH respectively, evidence in favour of the quinone-oxime structure of α-nitroso-β-naphthol has been presented. The spectrum of the copper chelate of α-nitroso-β-naphthol indicates a planar configuration of the complex with considerable resonance between the quinonoid and benzenoid structures of the ligand.

## RÉSUMÉ

On a effectué une étude des spectres d'absorption dans l'ultra-violet du β-naphtol, de l'α-nitroso-β-naphtol, et de son chélate avec le cuivre, en vue d'en établir la structure.

## ZUSAMMENFASSUNG

Es wird versucht, aus den U.V.-Absorptionsspektren von β-Naphthol und α-Nitroso-β-naphthol in saurem und alkalischem Medium sowie des Kupferkomplexes von α-Nitroso-β-naphthol Rückschlüsse auf deren Struktur zu ziehen.

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# THE DETERMINATION OF COBALT, IRON PLUS VANADIUM OR MANGANESE IN SOFT MAGNETIC ALLOYS

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Soft magnetic alloys have been developed which consist nominally of 48% of iron and cobalt and the balance of manganese or vanadium. These materials are useful because of their high saturation values. Vanadium and manganese have been added to facilitate the cold-working of the material.

The chemical analysis of these materials for iron, and manganese or vanadium is relatively simple. Iron may be determined conveniently by the conventional reduction with stannous chloride followed by titration with potassium dichromate using diphenylamine sulfonate as an indicator. Manganese may be determined by oxidation with peroxydisulfate in the presence of silver ion followed by the addition of a measured excess of ferrous sulfate and a back titration with potassium permanganate. Vanadium may be determined by the ferrous sulfate–peroxydisulfate method.

The determination of cobalt, however, presents some difficulty. Gravimetric methods are unattractive because of the high percentage of cobalt. The volumetric methods available for cobalt require a preliminary separation for these alloys.

In view of the successful application of ion exchange separations in conjunction with EDTA titrations in metallurgical analysis, a similar approach was taken for the determination of cobalt in these alloys.

The separation of iron and cobalt using a strongly basic anion exchange resin in hydrochloric acid medium has already been accomplished. KRAUSE AND MOORE have shown that manganese(II) and vanadium(IV) are not absorbed on a resin of this type in $9N$ hydrochloric acid[1,2]. Iron(III) and cobalt are both strongly absorbed under these conditions[3].

Solutions of cobalt, iron, manganese and vanadium were prepared so as to be able to approximate the content of an alloy by taking appropriate aliquots.

The solutions were standardized by adding somewhat more than the equivalent amount of EDTA and back titrating with a standard copper solution using calcein as fluorescent indicator[4]. The titrations were carried out under ultraviolet light using an apparatus previously described[4].

The column separation was performed by mixing appropriate aliquots of the standard solutions. The mixtures were evaporated nearly to dryness and diluted to approximately 10 ml with $9N$ hydrochloric acid. The solutions were transferred to an anion exchange column with $9N$ hydrochloric acid. Vanadium or manganese was eluted with $9N$ hydrochloric acid, cobalt with $4N$ hydrochloric acid, and iron with $0.5N$ hydrochloric acid. The values shown in Table I were obtained using the procedure given below for alloys.

TABLE I

| *Co present*[a] | *Co found* | *Fe present*[a] | *Fe found* | *V present*[a] | *V found* | *Mn present*[a] | *Mn found* |
|---|---|---|---|---|---|---|---|
| 51.8 | 51.8 | 32.2 | 32.1 | — | | 16.0 | 16.0 |
| 51.8 | 51.7 | 32.2 | 32.1 | — | | 16.0 | 16.0 |
| 51.8 | 51.8 | 32.2 | 32.4 | — | | 16.0 | 15.9 |
| 51.8 | 51.8 | 32.2 | 32.2 | — | | 16.0 | 16.1 |
| 51.8 | 51.7 | 32.2 | 32.2 | — | | 16.0 | 16.1 |
| 49.3 | 49.3 | 44.2 | 44.1 | 6.49 | 6.50 | — | |
| 49.3 | 49.2 | 44.2 | 44.2 | 6.49 | 6.53 | — | |
| 49.3 | 49.3 | 44.2 | 44.2 | 6.49 | 6.52 | — | |

[a] Nominal values for iron, vanadium and manganese by classical methods. Cobalt value by difference.

## PROCEDURE

Dissolve a 1-g sample in 10 ml of hydrochloric acid, $9N$. After the sample is dissolved add 5 drops of 30 vol.% hydrogen peroxide and boil for 10 min. Add 0.1 g of sodium sulfite and boil for 10 min. Transfer the solution to a 100-ml volumetric flask and dilute to volume with $9N$ hydrochloric acid. Transfer a 10-ml aliquot to an anion-exchange resin containing Dowex-1, (100–150 mesh, chloride form) previously washed with $9N$ hydrochloric acid. After rinsing the sample on to the resin elute the manganese or vanadium with 30 ml of $9N$ hydrochloric acid into a 250-ml beaker. Place a clean beaker under the column and elute with $4N$ hydrochloric acid until the blue cobalt band is removed from the column. After the cobalt has been removed from the column elute with $0.5N$ hydrochloric acid until the yellow iron band is removed.

Evaporate each fraction to a few ml, add 50 ml of water, and 10 ml of sodium

*References p. 429*

acetate–acetic acid buffer (for manganese, use ammonium acetate buffer). Add an excess of EDTA, adjust the pH to approximately 4.8 (Mn to pH of 7) and dilute to 150 ml with water. Add one drop of calcein (0.1% in 0.001$N$ NaOH) and back titrate with a standard copper solution to the quenching of the fluorescence of the free indicator. The titrations should be carried out with ultraviolet light as the sole source of illumination.

## DISCUSSION

The columns used for this work were constructed from a 1-cm diameter filter tube with a coarse frit. One end was flared and attached to one inch pyrex tubing three inches long so as to leave an eight inch section of tubing (resin bed), 1 cm in diameter between the frit and the large tubing. The tubing on the other side of the frit was reduced and attached to a 2-mm capillary stopcock. The stopcock was placed as close to the frit as possible. During the elutions the flow rate is controlled by the stopcock so as to allow one drop of solution every 4–6 sec.

The determination of cobalt and iron using EDTA is carried out most conveniently using calcein as an indicator and a standard copper solution as a back titrant. The determination of 50 mg of cobalt or iron in 150 ml of solution by this method presents no difficulty. Conventional indicators may be used but a smaller aliquot must be taken with a resultant larger error in the determination.

The iron, vanadium and manganese may be easily determined by other methods. However, the procedure developed for the cobalt determination also provides a convenient separation and determination of the other elements in these alloys.

## SUMMARY

A convenient ion exchange separation particularly designed for the separation of iron and vanadium or mangenese from cobalt has been developed for the determination of iron, cobalt and manganese or vanadium in soft magnetic alloys. After an anion exchange separation of their chloride complexes these elements are determined by a back titration of an excess of EDTA with a standard copper solution using calcein as an indicator under ultraviolet light.

## RÉSUMÉ

Une méthode de séparation par échange d'ions est proposée pour le dosage du fer et du cobalt, accompagnés de manganèse ou de vanadium. Après séparation, ces éléments sont dosés par titrage au moyen de l'acide éthylènediaminotétracétique en excès que l'on détermine avec une solution de cuivre étalon, en présence de calcéine comme indicateur.

## ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Eisen, Kobalt und Mangan oder Vanadium nach vorhergehender Trennung des Eisens und Vanadiums oder Mangans vom Kobalt mit Hilfe von Ionenaustauschern. Nach der Trennung werden diese Elemente durch Rücktitration eines zugesetzten Überschusses von Äthylendiamintetraessigsäure mit einer Standard-Kupfersalzlösung in Gegenwart von Calcein als Indikator bestimmt.

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# DETERMINATION OF URANIUM IN ZIRCON*

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## INTRODUCTION

One of the methods of measuring geologic time involves the quantitative determination of lead and uranium. The value of this method depends on both the accuracy and precision with which both lead and uranium can be determined.

In igneous rocks, the uranium and thorium content is generally higher in the accessory minerals than in the major rock forming minerals. Of the common accessory minerals, zircon usually has the highest uranium content, approximately 0.1%. The determination of uranium in zirconium minerals such as zircon is difficult by classical methods, especially if the sample is small. The extraction-fluorimetric method was adopted as the basis for analysis. The uranium is separated from interfering elements before preparation of the fluoride phosphor. This separation usually involves the solvent extraction or uranyl nitrate from $HNO_3$ solution after the addition of a salting agent. A portion of the solvent is then transferred to the standard container and after evaporation of the solvent, the phosphor is prepared. Vanadium, cerium(IV), thorium, and zirconium which are partly extracted cause quenching, especially if the ratios of these elements to uranium are large. This serious quenching effect of zirconium on the fluorescence of uranium is very pronounced in the intermediate-concentration (about 1000 p.p.m.) or low-concentration (about 100 p.p.m.) ranges.

Several investigators[1-3] have inhibited the extraction of zirconium from chromatographic columns by use of a number of anions, for example, phosphate, sulfate, oxalate, or tartrate as complexing agents. Precipitation with phosphate in high acid medium is a standard procedure for the separation of zirconium from other elements.

The purpose of this study was to obtain formal data on the effectiveness of phosphate as a retainer for zirconium in the extraction process and to develop a simple method for the determination of as little as 0.0005% of uranium in zircons.

### *Interference by zirconium*

The effect of varying amounts of zirconium on the fluorescences obtained for phosphors containing a known concentration of uranium is shown in Fig. 1. The effect of similar amounts of zirconium in the extraction method is shown in Fig. 2. Each reading is the average of replicate independent determinations. The data (Fig. 2) show that at a zirconium concentration around 10 μg/5 ml, sufficient zirconium is carried into the ethyl acetate phase to cause about 5% quenching of the uranium fluorescence. The interference by zirconium approaches a limiting value when the sample solutions contain more than 500 μg zirconium per 5 ml.

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* Publication authorized by the Director, U. S. Geological Survey.

### *Effect of phosphate concentration on uranium extraction*

The effect of phosphate concentration in absence of zirconium was first investigated. Solutions containing two levels of uranium and varying amounts of $Na_2HPO_4$ ranging from 0 to 100 mg were prepared in duplicate and processed through the extraction procedure. The data obtained from phosphors containing 0.12 μg and 0.30 μg U, respectively, are presented in Table I. The results show that as much as 100 mg of phosphate does not interfere in the extraction of uranyl nitrate with ethyl acetate. Plots of data, relating fluorescence to the uranium content, obtained with and without phosphate being present during the solvent extraction of uranyl nitrate, resulted in identical curves.

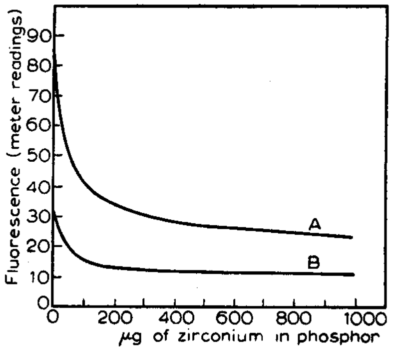

Fig. 1. The effect of zirconium upon the fluorescence of uranium-activated phosphor. Curve A, 0.3 μg U in phosphor. Curve B, 0.1 μg U in phosphor.

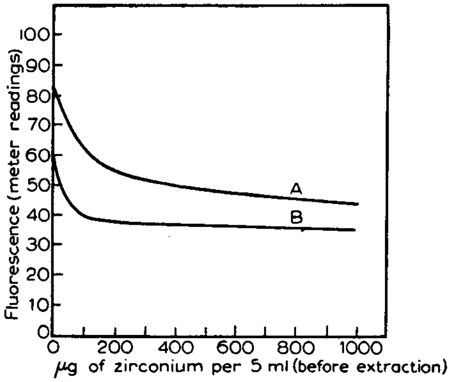

Fig. 2. The effect of zirconium upon the fluorescence of uranium-activated phosphor in the extraction method. Curve A, 0.3 μg U in phosphor. Curve B, 0.2 μg U in phosphor.

TABLE I

THE EFFECT OF VARYING AMOUNTS OF PHOSPHATE UPON THE SOLVENT EXTRACTION OF URANYL NITRATE

| *Phosphate (mg)* | *Fluorescence (meter readings)* 0.12 μg U in phosphor | *Fluorescence (meter readings)* 0.30 μg U in phosphor |
|---|---|---|
| none | 45, 45 | 90, 89 |
| 10 | 45, 45 | 90, 88 |
| 20 | 46, 46 | 89, 88 |
| 40 | 45, 45 | 90, 88 |
| 60 | 45, 45 | 90, 88 |
| 80 | 46, 46 | 89, 89 |
| 100 | 46, 45 | 90, 90 |

### *Separation of uranium from zirconium*

The presence of large amounts of zirconium is a major interference because of its partial extraction. Therefore, the extent of retention of zirconium by phosphate was investigated. Table II shows the fluorescence readings obtained for two series of solutions prepared in duplicate containing a known concentration of uranium (0.6 μg and 1.5 μg U, respectively), 50 mg $Na_2HPO_4$, and amounts of zirconium varying

TABLE II

SEPARATION OF URANIUM FROM ZIRCONIUM IN PRESENCE OF PHOSPHATE

| *Zirconium (µg)* | *Fluorescence (meter readings)* | |
|---|---|---|
| | *0.6 µg U in solution being extracted, 0.12 µg U in phosphor* | *1.5 µg U in solution being extracted, 0.3 µg U in phosphor* |
| none | 43, 44 | 91, 91 |
| 10 | 43, 44 | 91, 91 |
| 50 | 44, 43 | 92, 92 |
| 100 | 43, 43 | 92, 92 |
| 200 | 44, 44 | 91, 90 |
| 500 | 44, 44 | 90, 91 |
| 1000 | 43, 44 | 90, 91 |

up to 1 mg. The fluorescence readings show no significant change due to the presence of zirconium in the original solution. Additional studies made to determine the amount of zirconium retained in the aqueous phase by 50 mg $Na_2HPO_4$ during the solvent extraction showed that as much as 10 mg of zirconium was effectively retained. The order of addition of $Na_2HPO_4$ is important. Low recoveries of U resulted when the phosphate was added before the saturation of the sample solution with aluminum nitrate.

The data (Table II) also indicate that the recovery of uranium and its separation from zirconium is quantitative. Further tests showed that as little as 0.1 µg of uranium was quantitatively separated from 10 mg of zirconium (approximately a 1:100,000 U:Zr ratio).

## PROCEDURE

Grind the sample to an impalpable powder in a boron carbide mortar and mix thoroughly. Small particle size is necessary to insure complete fusion in a reasonable time. Weigh 0.1000 g sample into a 15-ml platinum crucible and add 1 g of carbonate–borate flux prepared by mixing equal portions by weight of anhydrous sodium carbonate and anhydrous sodium borate[4]. Mix thoroughly. Cover the crucible and place in a heated (150°–200°) furnace to drive off any moisture. Gradually increase the temperature until the mass is a viscous liquid (approximately 950°). Keep the crucible at this temperature for 20 to 30 min. Cool to room temperature and place the crucible and melt in a 100-ml beaker, add 15 ml (3+7) $HNO_3$, cover, and digest on a steam bath until the melt just dissolves. Transfer the solution quantitatively to a 50-ml volumetric flask removing and washing the crucible. Adjust the volume to 50 ml with water. The final nitric acid concentration is 7% v/v.

Place a 5-ml aliquot of sample solution in a 30-ml glass-stoppered test tube containing 9.5 g of low-uranium $Al(NO_3)_3 \cdot 9H_2O$. Place the tubes in a hot-water bath, and shake occasionally until solution is complete. Add 50 mg of solid $Na_2HPO_4$ and replace stoppered test tube in the hot-water bath in order to dissolve the phosphate. When solution is complete, cool the solution to room temperature or below.

Add 10 ml of ethyl acetate to the sample solution and transfer the stoppered test tubes together with rack to an automatic shaker, and then agitate for 5 min. Allow the phases to separate and carefully decant the supernatant ethyl acetate phase through a dry, dense, "ash-free" paper self-supported in the neck of a glass-stoppered test tube, thus removing any entrained water phase.

Pipette off a 2-ml aliquot of the filtrate and transfer to a special platinum dish[5] that is partly immersed in cold water. To prevent loss by creeping, immediately ignite the ethyl acetate by means of a small flame and allow the solvent to burn off. Then, heat the dishes on a hot plate or under an infra-red lamp at slightly above 100° until the residual liquid is evaporated.

Use the "fused" flux recommended by GRIMALDI, MAY, AND FLETCHER[5] containing 9% NaF, 45.5% $Na_2CO_3$, and 45.5% $K_2CO_3$ by weight. It has been found satisfactory for the measurement of fluorescence obtained from less than $10^{-8}$ g of uranium, and yields reproducible blanks at high instrumental sensitivity. Add 2 g of flux to each dish and place the dish in a dessicator until ready for fusion. Fusions are carried out in an apparatus[6] devised for preparing phosphors. The apparatus prepares 18 phosphors at a time and eliminates the tedious and time-consuming hand operation, while improving precision. Heat the samples for 8 min which is about 6 min longer then the melting time.

Cool the dishes on the apparatus for 10 min. Then, remove and place in a dessicator where they cool for 20 min before reading. Determine the fluorescence of the button using a reflection fluorimeter[5] if the sample contains more than 0.01% U and using a Model VI transmission fluorimeter[7] if the sample contains less than 0.01% U. Obtain the uranium content of each button by comparison of its fluorescent intensity with that from buttons obtained from known solutions cycled through the modified procedure.

## RELIABILITY OF RESULTS

A series of synthetic samples were prepared to obtain reproducibility data for the procedure. The results of these tests are presented in Table III. Results of analyses have an accuracy of 97–98% of the contained uranium and a standard deviation of less than 2.5%. Samples of zircon were also analyzed using the original fluorimetric method and the modified procedure. The comparative data (Table IV) show that low results are obtained when the phosphate retainer is omitted from the procedure.

TABLE III

RELIABILITY OF RESULTS (0.12 μg U)

| *μg Uranium found (extracted in presence of 5 mg Zr)* | *μg Uranium found (extracted in presence of 10 mg Zr)* |
|---|---|
| 0.118 | 0.118 |
| 0.118 | 0.124 |
| 0.124 | 0.126 |
| 0.124 | 0.126 |
| 0.120 | 0.120 |
| 0.118 | 0.120 |
| 0.118 | 0.120 |
| 0.120 | 0.120 |
| 0.118 | 0.120 |
| 0.120 | 0.120 |
| 0.118 | 0.126 |
| 0.120 | 0.120 |
| Average = 0.1196<br>Standard deviation = 0.0021<br>% Standard deviation = 1.8 | Average = 0.1220<br>Standard deviation = 0.0028<br>% Standard deviation = 2.3 |

TABLE IV

ANALYSIS OF ZIRCON

| *Zircon* | *Uranium content (p.p.m.)*<br>*without phosphate* | <br>*with phosphate* |
|---|---|---|
| Original SS-S-487-8[a] | 430 | 550 |
| Leached SS-S-487-8[a] | 330 | 420 |
| Original SS-S-487-9[a] | 105 | 123 |
| Leached SS-S-487-9[a] | 78 | 93 |
| 120-BNH-36[b] | 2430 ± 10 | 2610 ± 10 |
| 198-BNH-72[b] | 2390 ± 10 | 2590 ± 10 |
| 189-BNH-64[b] | 7730 ± 10 | 7880 ± 10 |

[a] Analyses by Alice Caemmerer, U. S. Geological Survey, Wash., D. C.
[b] Analyses by Marian Schnepfe, U. S. Geological Survey, Wash., D. C.

## CONCLUSIONS

Routine fluorimetric analyses for uranium in zircons can be accomplished rapidly and accurately using $Na_2HPO_4$ as a retainer for zirconium. The standard deviation obtained from routine replicate analyses performed in this manner is less than 2.5% when uranyl nitrate is solvent-extracted in the presence of approximately 100,000 times the amount zirconium. The conditions described in the modified procedure have proved valuable in the separation of $\mu$g amounts of uranium from large amounts of zirconium.

## ACKNOWLEDGEMENT

This work is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Research of the U. S. Atomic Energy Commission.

## SUMMARY

A routine fluorimetric procedure is described for the determination of trace amounts of uranium in zircon. It employs the direct extraction of uranyl nitrate with ethyl acetate using phosphate as a retainer for zirconium. Submicrogram amounts or uranium are separated in the presence of 100,000 times the amount of zirconium. The modified procedure has been worked out using synthetic mixtures of known composition and zircon. Results of analyses have an accuracy of 97–98% of the contained uranium and a standard deviation of less than 2.5%.

## RÉSUMÉ

Une méthode fluorimétrique est proposée pour le dosage de traces d'uranium dans un zircon. On procède à l'extraction directe du nitrate d'uranyle, au moyen d'acétate d'éthyle.

## ZUSAMMENFASSUNG

Es wird eine fluorimetrische Methode zur Bestimmung von Spuren von Uran in Zirkonium beschrieben. Sie beruht auf einer direkten Extraktion von Uranylnitrat mit Äthylacetat.

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# SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF COBALT, NICKEL AND COPPER WITH N,N'-BIS(3-DIMETHYLAMINOPROPYL)DITHIO-OXAMIDE

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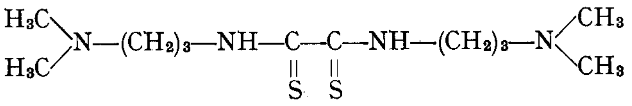
## INTRODUCTION

In a recent study of a series of substituted dithio-oxamides[1] it was found that one derivative, N,N'-bis(3-dimethylaminopropyl)dithio-oxamide, showed promise of being a good reagent for the simultaneous spectrophotometric determination of cobalt, nickel and copper. This reagent has been investigated fully to see if it has any advantages over dithio-oxamide (rubeanic acid)[2] as a reagent for these three metal ions.

N,N'-bis(3-dimethylaminopropyl)dithio-oxamide has the following structure:



$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!N-(CH_2)_3-NH-\underset{\underset{S}{\|}}{C}-\underset{\underset{S}{\|}}{C}-NH-(CH_2)_3-N\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

I

The same dissociation and tautomerism equilibria may be postulated for this compound as was done in the case of dithio-oxamide. A high concentration of the active anionic form of the reagent is achieved by removal of $H^+$ ions, *i.e.*, by the addition of hydroxide ions.

Compound I is subject to fewer interfering ions than is dithio-oxamide and the effect of the nickel to cobalt ratio is not as great a factor in the determination as is the case in the dithio-oxamide procedure.

The sensitivities of the cobalt and copper color reactions of Compound I are comparable to the respective reactions with dithio-oxamide. The sensitivity of the nickel reaction with the reagent is about 10% less than the corresponding reaction with dithio-oxamide.

## APPARATUS

### *Spectrophotometers*

Beckman spectrophotometers, Model DK-2 and Model DU, with matched 1-cm Corex cells were used.

### *pH Meter*

A Beckman pH meter, Model G, was employed for all pH measurements. It was calibrated with Fisher certified standard buffers.

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*References p. 443*

## REAGENTS

*Standard cobalt solution*

A solution containing 1 mg cobalt/ml was prepared by dissolving 2.03 g of cobalt chloride hexahydrate in doubly-distilled water. Twice distilled hydrochloric acid was added so that the final concentration, after dilution to 500 ml, was one molar. The solution was standardized electrolytically.

*Standard nickel solution*

A standard nickel solution containing 1 mg nickel/ml was prepared by dissolving 2.03 g of nickel chloride hexahydrate in the above manner. The solution was standardized by the dimethylglyoxime gravimetric method.

*Standard copper solution*

A copper solution containing 1 mg copper/ml was prepared by dissolving 1.45 g of cupric chloride dihydrate in the above manner. The solution was standardized electrolytically.

*Buffer solutions*

A pH-9 buffer was prepared by dissolving 3.84 g of sodium borate decahydrate in 1 l of doubly-distilled water and a pH-4 buffer by dissolving 1.01 g of potassium acid phthalate in 100 ml of doubly-distilled water. All other buffers were prepared according to the directions given by BRITTON[3].

*N,N′-bis(3-dimethylaminopropyl)dithio-oxamide solution*

A $1.5 \cdot 10^{-3} M$ solution of this reagent was prepared by dissolving 43.5 mg in 100 ml of 95% ethanol.

*Gum acacia solution*

A 0.1% solution of gum acacia was prepared by dissolving 0.2 g in 200 ml of doubly-distilled water.

*Doubly-distilled water*

All water used in this work was distilled twice and finally run through a cation-exchange resin, Amberlite IR-120. The resin column was 26 cm in length and had an internal diameter of 2 cm.

*Other reagents*

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

## EXPERIMENTAL

### *Properties of the reagent*

N,N′-bis(3-dimethylaminopropyl)dithio-oxamide is a yellow solid which is more soluble in ethanol than the parent compound. An ethanolic solution of the reagent is pale yellow. The absorbance curve of a $1.2 \cdot 10^{-4} M$ solution is shown in Fig. 1. In practice a $1.5 \cdot 10^{-3} M$ reagent solution is employed so that the useful range of metal ion concentrations may conveniently be used and still have a sufficient excess of reagent.

The reagent solution is stable to light, hydrolysis, and oxygen and carbon dioxide of the air for at least a month. Absorbance measurements on the reagent solution showed no significant change over this period; measurements were not made over a longer time.

### *Properties of the complexes*

*Color.* Cobalt, nickel and copper form water-insoluble complex salts with the reagent solution. The cobalt complex is yellow, the nickel complex reddish orange and the copper complex olive green. A protective colloid keeps the complexes in solution over the concentration range used. Gum acacia and gelatin are the substances generally used for this purpose. Gelatin solutions are stable for about a week, whereas gum acacia solutions a month old were just as effective in keeping the complexes in solution as ones freshly prepared. Consequently, gum acacia was the protective colloid used in this work. Absorbance curves of 2.00 p.p.m. solutions of the complexes are shown in Fig. 1. The absorbances of the complexes were measured against a reagent blank. The nickel and copper complexes have a maximum at 500 mμ and 365 mμ, respectively, while the cobalt complex has a broad adsorbance peak with the maximum occurring at 350 mμ. At 430 mμ the sensitivity of the cobalt reaction is about 2% less than at 350 mμ. Since the absorbance due to the reagent, the nickel and copper complexes are less at 430 mμ than at 350 mμ, the former is the most advantageous wavelength to use when simultaneous determinations are to be made.

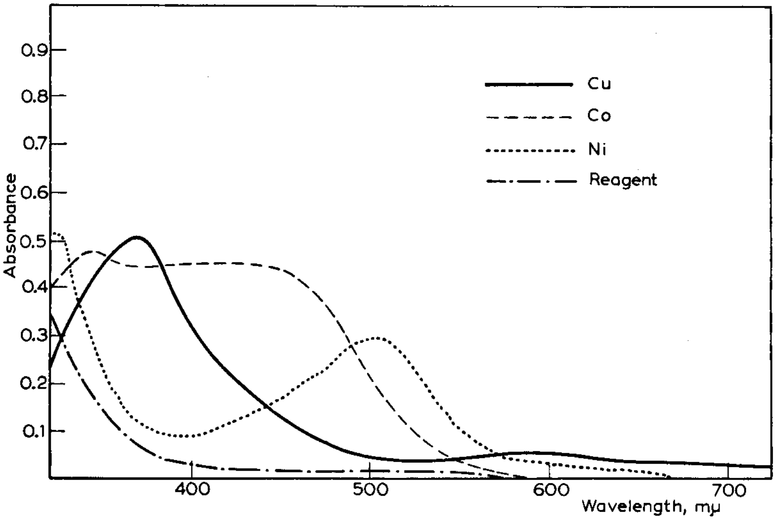


Fig. 1. Absorbance curves of 2.00 p.p.m. solutions of the cobalt, nickel and copper complexes. Reagent curve, $1.2 \cdot 10^{-4} M$. All at pH 9.

*Effect of pH.* The effect of the hydrogen-ion concentration is shown in Fig. 2. The absorbance curves were obtained by using 1.60 p.p.m. of the ion, 4 ml of a 0.1% gum acacia solution, 10 ml of a buffer solution of the desired pH and 3 ml of the reagent solution. The samples were diluted to 25 ml with distilled water and absorbance measurements made against a reagent blank. From the curves it is seen that the optimum pH for making simultaneous measurements is 9.0 ± 0.3.

*Rate of color formation.* The cobalt and nickel complexes require 30 min for maximum color development at 20°. The rate of color formation was found to vary from 35 min at 15° to 20 min at 35°. The copper complex on the other hand exhibits maximum color development at once. Temperature studies made at 15°, 20°, and 35° on the copper complex showed the absorbance to be at a maximum when the first measurement was made. Since the rate of reaction in the case of the cobalt and nickel complexes was not greatly increased at 35°, all determinations were made at room temperature and the color allowed to develop for 30 min.

*Structure of the complexes in solution.* The empirical formulas of the three complexes *in solution* were established by the mole ratio method of YOE AND JONES[4] and the continuous variations method of JOB[5] as modified by VOSBURG AND COOPER[6]. The results of these two methods applied to the cobalt complex are shown in Figs. 3 and 4. They indicate a ratio of 2 moles of cobalt to 3 moles of reagent. This corresponds to a salt of $Co^{+3}$ and reagent having the formula:

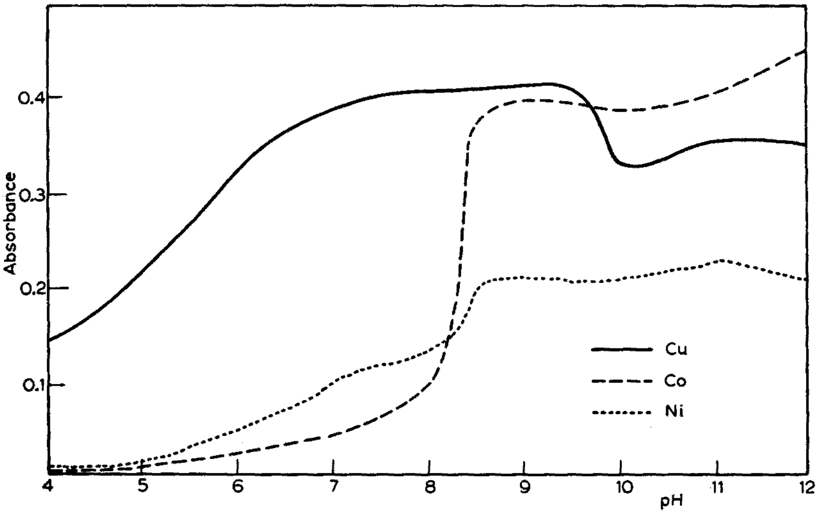


Fig. 2. Effect of pH on the cobalt, nickel and copper complexes.

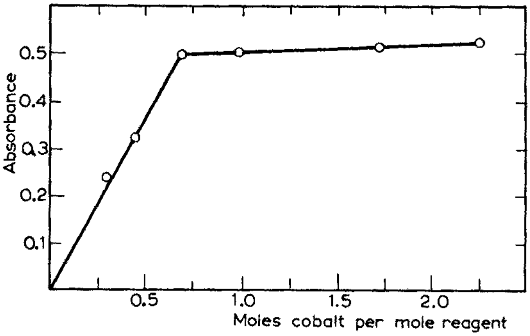
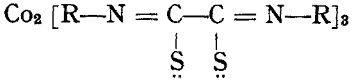
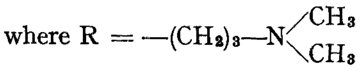


Fig. 3. Mole ratio method applied to cobalt complex, pH 9, 430 m$\mu$.



$$Co_2\,[R{-}N = \underset{\underset{\cdot\cdot}{S}}{\overset{}{C}}{-}\underset{\underset{\cdot\cdot}{S}}{C} = N{-}R]_3$$



$$\text{where } R = {-}(CH_2)_3{-}N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$$

*References p. 443*

Nickel and copper each combine in ratios of one mole ion to one mole reagent, indicating that salts are formed by $Ni^{+2}$ and $Cu^{+2}$ reacting with the divalent N,N'-bis-(3-dimethylaminopropyl)dithio-oxamate anion.

*Order of addition of reagents.* The solutions containing the metallic ion and protective colloid must be adjusted to the proper pH before addition of the reagent solution if maximum sensitivity is to be attained.

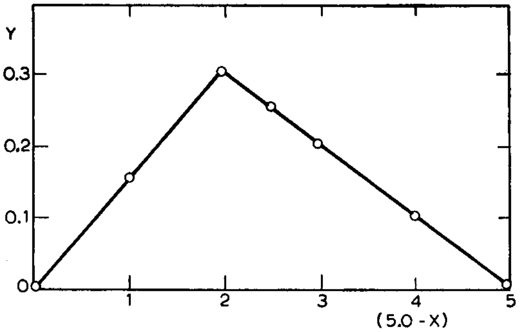


Fig. 4. Continuous variations method applied to cobalt complex, pH 9, 430 mμ.

*Adherence to Beer's law.* Samples containing varying concentrations of the metallic ion, 4 ml gum acacia solution, 10 ml pH 9 buffer and 3 ml reagent solution were allowed to develop for 30 min after which they were diluted to 25 ml with distilled water. The absorbances of these solutions were measured against a reagent blank at wavelengths of 430 mμ, 500 mμ and 365 mμ for the complexes of cobalt, nickel and copper, respectively. Beer's law is obeyed by all three systems over the range 0.16 p.p.m. to 4.00 p.p.m. Lower and higher concentrations were not investigated.

*Effect of diverse ions.* Palladium is the only ion that reacts with N,N'-bis(3-dimethylaminopropyl)dithio-oxamide in alkaline medium exclusive of cobalt, nickel and copper. It was found to produce a change in absorbance of 0.010 unit in the measurement of the cobalt complex when present in ratios of 1:1 or more. Higher tolerances may be allowed in the determination of copper and nickel but since the procedure is for the analysis of all three ions, the limiting concentration of palladium is determined by its effect on the cobalt complex.

The cyanide ion must be absent because it forms more stable complexes with cobalt, nickel and copper than does the reagent. High concentrations of citrate and tartrate ions, *i.e.*, concentrations high enough to prevent the precipitation of iron and aluminum at pH 9, interfere in the determination of all three ions.

Ions such as $Fe^{+3}$, $Al^{+3}$, $Mn^{+2}$, etc. which precipitate in alkaline solution must be absent, or, if present, must either be removed or complexed to prevent their interference.

*Sensitivity.* The sensitivities of the color reactions as defined by SANDELL[7] are as follows:

for cobalt at 430 mμ, 0.0045 $\gamma/cm^2$
for nickel at 500 mμ, 0.0077 $\gamma/cm^2$
for copper at 365 mμ, 0.0039 $\gamma/cm^2$.

Practical sensitivities based upon an absorbance of 0.005 unit are 0.025 p.p.m. cobalt, 0.039 p.p.m. nickel and 0.020 p.p.m. copper.

*Simultaneous determination of cobalt, nickel and copper.* Table I lists the values of the molar extinction coefficients of the complexes of cobalt, nickel and copper measured at wavelengths of 430 mμ, 500 mμ and 365 mμ, respectively. These values may be used to derive equations for the determination of one or more components[8]. The equations derived from these values are given in Table II. It was found that the presence of cobalt does not result in a shift of the absorbance peak of the nickel complex as is the case with dithio-oxamide. However, the absorbance curve of the nickel complex is altered by the presence of cobalt in such a way that the molar extinction coefficients of the nickel complex at 430 mμ and 365 mμ, respectively, are different from the values calculated on the basis of the nickel complex alone. Fig. 5 shows the absorbance curves of a 2.00 p.p.m. solution of the nickel complex alone and in the presence of 1.00 p.p.m. cobalt. Consequently, two values of the molar extinction coefficients of the nickel complex, at 430 mμ and at 365 mμ, must be considered. In Table I the values of the molar extinction coefficients of the nickel complex formed in the presence of cobalt are given in parenthesis.

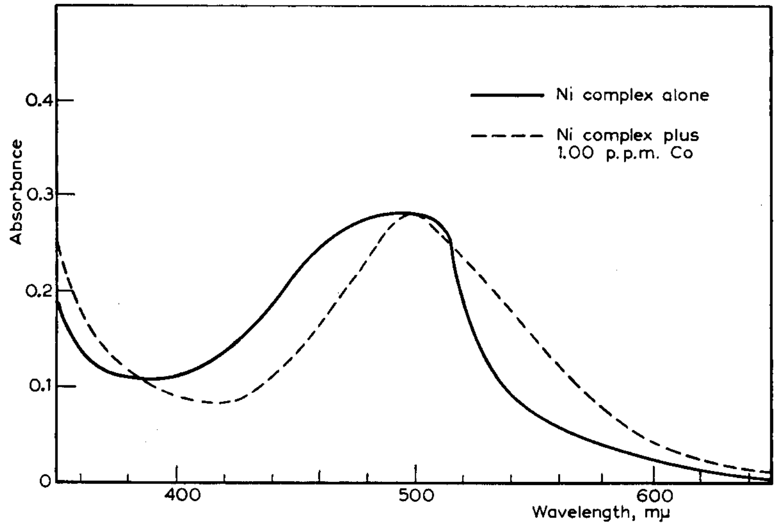


Fig. 5. Effect of cobalt on the nickel complex.

*Recommended procedure.* The optimum conditions for the determination of cobalt, nickel and copper are those under which the absorbances of the complexes are the highest, the most stable and the most reproducible. These conditions are fulfilled by measuring the absorbance of a solution at 500 mμ, 430 mμ, and 365 mμ respectively, against a reagent blank containing 2 ml of reagent solution, which has been prepared as follows: the complexes are formed at a pH of 9.0 ± 0.3 in the presence of 4 ml of a 0.1% gum acacia solution by adding 3 ml of a $1.5 \cdot 10^{-3} M$ reagent solution. Allow the sample 30 min for maximum color development. Dilute to 25 ml, mix and measure the absorbances at the indicated wavelengths. The molar concentrations of the ions are then calculated by using the spectrophotometric equations in Table II.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF THE COBALT, NICKEL AND COPPER COMPLEXES

| *Co* | *365 mμ* | *430 mμ* | *500 mμ* |
|---|---|---|---|
| $\varepsilon$Co | 14,000 | 14,500 | 6,450 |
| $\varepsilon$Ni | 3,140 (4,700) | 4,070 (2,640) | 7,150 |
| $\varepsilon$Cu | 15,000 | 4,580 | 1,970 |

TABLE II

SPECTROPHOTOMETRIC EQUATIONS

*One of three ions present*

$$(\mathrm{Co})\cdot 10^5 = 6.89\, A_s\, 430$$
$$(\mathrm{Ni})\cdot 10^5 = 14.0\, A_s\, 500$$
$$(\mathrm{Cu})\cdot 10^5 = 6.67\, A_s\, 365$$

*Two of three ions present*

$$(\mathrm{Co})\cdot 10^5 = 8.03\, A_s\, 430 - 2.63\, A_s\, 500$$
$$(\mathrm{Ni})\cdot 10^5 = 16.3\, A_s\, 500 - 7.25\, A_s\, 430$$

$$(\mathrm{Co})\cdot 10^5 = 9.75\, A_s\, 430 - 2.97\, A_s\, 365$$
$$(\mathrm{Cu})\cdot 10^5 = 9.42\, A_s\, 365 - 9.08\, A_s\, 430$$

$$(\mathrm{Ni})\cdot 10^5 = 14.8\, A_s\, 500 - 1.95\, A_s\, 365$$
$$(\mathrm{Cu})\cdot 10^5 = 7.08\, A_s\, 365 - 3.10\, A_s\, 500$$

*Three ions present*

$$(\mathrm{Co})\cdot 10^5 = 10.6\, A_s\, 430 - 2.99\, A_s\, 365 - 1.95\, A_s\, 500$$
$$(\mathrm{Ni})\cdot 10^5 = 16.6\, A_s\, 500 - 7.50\, A_s\, 430 + 0.11\, A_s\, 365$$
$$(\mathrm{Cu})\cdot 10^5 = 9.03\, A_s\, 365 - 7.46\, A_s\, 430 - 3.37\, A_s\, 500$$

*Analysis of synthetic samples and NBS standard samples.* A series of synthetic samples and three National Bureau of Standards samples were analysed by the above procedure. Each sample had the indicated ion concentration, 4 ml of a 0.1% gum acacia solution, 3 drops of a 0.1% thymolphthalein solution and was adjusted to a pH 9.0 ± 0.3 with sodium hydroxide and hydrochloric acid until the blue color of the indicator just turned colorless. Ammonium hydroxide must not be used because the presence of high concentrations of ammonium ions prevent the development of the nickel complex. 3 ml of a $1.5\cdot 10^{-3}M$ reagent was added and the samples given 30 min for maximum color development. The samples were diluted to the mark in 25-ml volumetric flasks, mixed and the absorbances measured at the respective wavelengths against a reagent blank which contained 2 ml of reagent solution. The results are given in Tables III and IV.

In order to prevent precipitation of the hydrated oxides of aluminum and iron when the NBS samples 85a, 87 and 58 were analysed, the aluminum was complexed

## TABLE III

ANALYSIS OF SYNTHETIC SAMPLES

| *Sample* | *Added (p.p.m.)* | *Found (p.p.m.)* |
|---|---|---|
| 1 | Ni 1.00 | 1.08 |
| | Cu 2.50 | 2.52 |
| 2 | Ni 1.70 | 1.72 |
| | Cu 1.50 | 1.51 |
| 3 | Ni 2.35 | 2.34 |
| | Cu 1.00 | 1.09 |
| 4 | Co 2.50 | 2.47 |
| | Cu 1.00 | 0.98 |
| 5 | Co 1.50 | 1.36 |
| | Cu 1.70 | 1.62 |
| 6 | Co 1.00 | 1.08 |
| | Cu 2.30 | 2.37 |
| 7 | Co 0.90 | 0.94 |
| | Ni 2.50 | 2.45 |
| 8 | Co 1.40 | 1.37 |
| | Ni 1.30 | 1.33 |
| 9 | Co 2.50 | 2.30 |
| | Ni 0.80 | 0.92 |
| 10 | Co 1.00 | 0.89 |
| | Ni 2.00 | 1.97 |
| | Cu 0.80 | 0.84 |
| 11 | Co 0.50 | 0.48 |
| | Ni 1.50 | 1.55 |
| | Cu 1.60 | 1.55 |
| 12 | Co 2.00 | 1.92 |
| | Ni 0.50 | 0.39 |
| | Cu 1.20 | 1.29 |
| 13 | Co 0.40 | 0.37 |
| | Ni 0.80 | 0.86 |
| | Cu 2.50 | 2.54 |

## TABLE IV

ANALYSIS OF NATIONAL BUREAU OF STANDARDS SAMPLES

| *Material* | *NBS Value* % | *Found* | |
|---|---|---|---|
| | | % *Ni* | % *Cu* |
| Al alloy, 85a | Ni 0.41 | 0.44 | 2.41 |
| | Cu 2.48 | 0.38 | 2.50 |
| | | 0.40 | 2.43 |
| | | 0.35 | 2.38 |
| | av. | 0.39 | 2.43 |

TABLE IV (Continued)

| *Material* | *NBS Value* % | *Found* | |
|---|---|---|---|
| | | % *Ni* | % *Cu* |
| Al–Si alloy, 87 | Ni 0.59 | 0.53 | 0.28 |
| | Cu 0.30 | 0.55 | 0.31 |
| | | 0.56 | 0.29 |
| | | 0.54 | 0.28 |
| | | av. 0.55 | 0.29 |
| Fe–Si alloy, 58 | Ni 0.115 | 0.103 | 0.037 |
| | Cu 0.04 | 0.105 | 0.033 |
| | | 0.108 | 0.035 |
| | | 0.105 | 0.038 |
| | | av. 0.105 | 0.036 |

with 5 ml of a 5%-sodium fluoride solution in the case of aluminum alloys 85a and 87 and the iron in the ferro-silicon alloy 58 was extracted with diethyl ether from a 20% hydrochloric acid solution.

## ACKNOWLEDGEMENT

The authors wish to express their thanks to the Mallinckrodt Chemical Works for their gift of the N,N'-bis(3-dimethylaminopropyl)dithio-oxamide used in this work.

## SUMMARY

The cobalt, nickel and copper complexes of N,N'-bis(3-dimethylaminopropyl)dithio-oxamide have been characterized in terms of color, effect of pH, rate of color formation, structure *in solution*, order of addition of reagents, adherence to Beer's law, and sensitivity. The reactivity of the reagent to other ions has been reported. A method for the simultaneous spectrophotometric determination of cobalt, nickel and copper has been developed. The results of the application of this procedure to synthetic samples and to several National Bureau of Standards samples are given.

## RÉSUMÉ

Les complexes du cobalt, du nickel et du cuivre avec la N,N'-bis(diméthylamino-3-propyle) dithioxamide ont été étudiés. Une méthode spectrophotométrique est proposée pour le dosage de ces trois éléments.

## ZUSAMMENFASSUNG

Es werden die Komplexverbindungen von Kobalt, Nickel und Kupfer mit N,N'-bis(3-dimethylamino-propyl)dithiooxamid beschrieben und über eine spektrophotometrische Methode zur Bestimmung dieser drei Elemente berichtet.

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# UN DOSAGE TRÈS SÉLECTIF DU NICKEL AVEC LA CYCLOHEXANEDIONEDIOXIME

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## INTRODUCTION

Nous nous proposons d'établir une méthode de séparation et de dosage du nickel dans un mélange renfermant un grand nombre de cations et plus particulièrement du cobalt en très forte quantité. Ce travail comprend trois parties; l'une a pour objet la séparation du nickel des autres cations par extraction, la seconde traite du dosage du nickel par la nioxime et dans la troisième, nous proposons quelques applications.

Pour ce travail nous utiliserons le chlorure de nickel Merck „cobalt frei" et la nioxime, préparée par la maison Fluka, selon la méthode RAUH *et al.*[1] dont le point de fusion est de 185°.

## SÉPARATION DU NICKEL PAR EXTRACTION

### (*a*) *Extraction du nickel*

*Solutions utilisées.* Chlorure de nickel 0.01$M$, nioxime 0.01$M$, solution tampon pH 7 (50 ml de $KH_2PO_4$ $M/5$ + 29.63 ml de NaOH $N/5$ complété à 200 ml par addition d'eau bidistillée), acide chlorhydrique 5$N$.

*Mode opératoire.* Dans un tube à centrifuger, on introduit 2 ml de tampon, 0.5 ml d'un solvant non miscible à l'eau, on agite trois minutes, chauffe à 80° pendant 5 min, laisse refroidir à 20° et centrifuge. Trois cas peuvent se présenter: Le précipité de nickel-nioxime reste dans la solution aqueuse (phénomène indiqué dans le Tableau I

TABLEAU I

COMPORTEMENT DES COMPLEXES Fe, Co ET Ni-NIOXIME DANS DIVERS SOLVANTS ORGANIQUES

| *Solvants* | *Fe-nioxime* | *Co-nioxime* | *Ni-nioxime* |
|---|---|---|---|
| Alcool benzylique | soluble | soluble | soluble |
| Cyclohexanol | insoluble | soluble | suspension |
| Méthylcyclohexanol | insoluble | soluble | suspension |
| Méthyléthylcétone | soluble | soluble | suspension |
| Benzène | insoluble | insoluble | suspension |
| Toluène | insoluble | insoluble | suspension |
| Cyclohexanone | insoluble | soluble | suspension |
| Quinoléine | soluble | soluble | soluble |
| Trichloréthylène | insoluble | insoluble | suspension |
| Cyclohexane | insoluble | insoluble | suspension |
| Chloroforme | insoluble | insoluble | suspension |
| Pentachloréthane | insoluble | insoluble | suspension |
| Éther | insoluble | insoluble | suspension |
| Alcool amylique | insoluble | insoluble | suspension |
| Phénol | insoluble | insoluble | soluble |

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sous le terme de „insoluble"). Le précipité se dissout dans le solvant (soluble) ou enfin le précipité passe quantitativement dans le solvant à l'état du suspension ou de précipité (suspension).

Comme le montre le Tableau I, il ne nous a pas été possible de trouver un solvant susceptible de dissoudre la nickel-nioxime seule. Une partie du fer et du cobalt sont extraits avec le nickel. On peut par contre séparer le cobalt du fer avec la cyclohexanone et le cyclohexanol. Mais il est possible de séparer le nickel du fer et du cobalt par un processus peu usuel en analyse mais qui donne, dans notre cas, d'excellents résultats. Il s'agit de faire passer quantitativement la nickel-nioxime, à l'état solide, dans la phase organique. On obtient celle-ci soit en suspension, soit sous forme d'un précipité qui se rassemble à la surface de séparation des deux liquides mais quantitativement dans la phase organique. Les deux autres cations restent dans l'eau à l'état dissous ou de précipité. L'étude de ce phénomène s'est effectuée de la façon suivante On introduit 5 ml de tampon pH 7, 0.5 ml de la solution de $NiCl_2$ $0.01M$ et 1 ml de nioxime $0.0563M$. On attend 10 min, le complexe est alors extrait par le solvant organique et la phase aqueuse séparée après centrifugation. Le solvant organique est traité par 5 ml d'une solution chlorhydrique $5N$ qui détruit le complexe lorsqu'on agite. Le nickel ne passe dans la solution aqueuse quantitativement. On sépare les deux liquides et on lave trois fois le solvant organique avec 5 ml d'eau distillée. Les résultats de quelques essais sont donnés dans le Tableau II.

TABLEAU II

| *μg Ni ajouté* | *Solvant utilisé* | *μg Ni trouvé* | *Erreur en %* |
|---|---|---|---|
| 292.5 | Trichloréthylène | 290 | 0.8 |
| 292.5 | Toluène | 291 | 0.8 |
| 292.5 | Alcool amylique | 288 | 1.3 |
| 292.5 | Benzène | 292 | 0.3 |
| 292.5 | Cyclohexanol | 291 | 0.8 |

Comme on le voit, les pertes sont de l'ordre de 1%. Le dosage colorimétrique du nickel a été fait dans la phase aqueuse par la méthode de FERGUSON ET BANKS[2].

*Sélectivité et extraction.* Nous indiquons, dans le Tableau IV, les cations gênants le dosage direct du nickel au pH de 3.5 (pH pour lequel le Ni-nioxime précipite encore quantitativement).

Nous avons effectué l'extraction du nickel, selon le processus indiqué ci-dessus, en prenant le benzène comme liquide extracteur, le dosage du nickel a été effectué par la méthode FERGUSON ET BANKS[2].

TABLEAU III

IONS INTERFÉRANT APRÈS EXTRACTION AU BENZÈNE

*Ions interférant même en petite proportion:* $Pd^{+2}$, $Bi^{+3}$, $Sn^{+2}$, $Sb^{+3}$, $Hg_2^{+2}$.

*Ions ne gênant pas à faible concentration:* $Cr^{+6}$, $Pb^{+2}$.

*Les ions suivants n'interfèrent pas, même s'ils sont présents en forte proportion:* $Ag^+$, $Cd^{+2}$, $As^{+3}$, $As^{+5}$, $Cu^{+2}$, $Co^{+2}$, $Fe^{+2}$, $Fe^{+3}$, $Mn^{+2}$, $Mn^{+7}$, $Al^{+3}$, $Cr^{+3}$, $Zn^{+2}$, $Mg^{+2}$, $Ca^{+2}$, $Ba^{+2}$, $Sr^{+2}$, $Li^+$, $K^+$, $Na^+$, $NH_4^+$, $U^{+6}$, $Mo^{+6}$.

TABLEAU IV

ORIGINE DE L'INTERFÉRENCE DUE À DIVERS IONS

*Ions réagissant avec la nioxime au pH de 3.5:*

| | |
|---|---|
| $Cu^{+2}$ , | complexe brun jaune, soluble en milieu aqueux |
| $Fe^{+2}$ , | complexe brun rouge, soluble en milieu aqueux |
| $Fe^{+3}$ , | complexe brun foncé, soluble en milieu aqueux |
| $Co^{+2}$ , | complexe brun jaune, soluble en milieu aqueux |
| $Bi^{+3}$ , | complexe jaune, insoluble en milieu aqueux |
| $Pd^{+2}$ , | complexe jaune, insoluble en milieu aqueux |
| $Ni^{+2}$ , | complexe rouge carmin, insoluble en milieu aqueux |

*Ions précipitant au pH de 3.5:*

| | |
|---|---|
| $Fe^{+3}$ , | précipitation de l'hydroxyde brun |
| $Bi^{+3}$ , | précipitation d'un sel basique, BiOCl |
| $Sn^{+2}$ , | précipitation de l'hydroxyde |
| $Sb^{+3}$ , | précipitation d'un sel basique, SbOCl |
| $Hg_2{}^{+2}$ , | dismutation en HgO et Hg |

*Ions colorant la solution aqueuse:*

| | |
|---|---|
| $Cr^{+6}$ , | coloration jaune de la solution |
| $Mn^{+7}$ , | coloration violette de la solution |
| $UO_2{}^{+2}$ , | coloration jaune de la solution |

Cette méthode d'extraction des ions gênant le dosage colorimétrique du nickel par la nioxime est très sélective, tout en étant rapide. Elle exige peu de manipulations, ce qui réduit les causes d'erreurs dues aux pertes de substance.

### b) *Extraction du nickel dans un système refermant une très grande quantité de cobalt*

Dans ces conditions, la technique décrite ci-dessus ne convient pas, car elle est longue et onéreuse; il faut de grandes quantités de nioxime pour complexer le cobalt; d'autre part elle n'est plus quantitative lorsque celui-ci est en trop fortes proportions ($<$ 1/100). Nous proposons donc une préextraction du cobalt (qui ne doit pas nécessairement être quantitative) dans un solvant organique, au moyen du thiocyanate. Nous avons choisi tout d'abord comme solvant le mélange éther–amylol utilisé en colorimétrie. Mais pour que le nickel reste quantitativement dans la phase aqueuse au cours de l'extraction du cobalt, il est nécessaire que celle-ci soit suffisamment acide.

Or, au cours des extractions successives du cobalt, nous avons constaté une diminution très forte de l'acidité de la solution aqueuse, probablement par suite du passage de l'acide thiocyanique non dissocié dans le solvant organique. Cette augmentation de pH n'est pas favorable à la séparation, car une partie du nickel passe alors dans la phase organique avec le cobalt. Par contre, si on part d'une solution très acide, les pertes en nickel sont négligeables, mais l'extraction du cobalt est plus difficile et exige d'importantes quantités de solvant. Nous avons donc porté notre choix sur un autre solvant, l'acétate d'éthyle, qui permet d'effectuer une élimination rapide du cobalt sans perte de nickel en partant d'une solution aqueuse HCl 5*N*.

*Appareillage et mode opératoire.* L'extraction selon la technique habituelle n'ayant pas donné satisfaction (on observe des pertes en nickel pouvant aller jusqu'à 5%) nous avons mis au point un dispositif qui est une modification de l'appareil de KIRK[3] (Fig. 1).

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*Position des robinets au départ*: 1 et 2 sont tournés de façon à assurer le passage de la solution de A à B, 1 étant fermé par rapport à F.

Le robinet 3 étant fermé, on tourne 4 et 5 de façon à ce que l'on puisse aspirer l'air à travers B au moyen de la trompe à vide D. 4 est fermé par rapport à C.

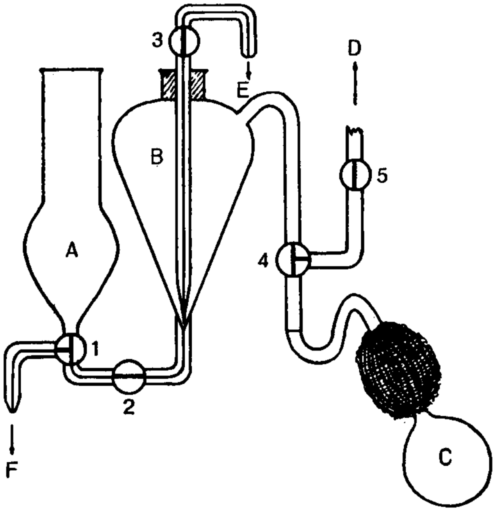

Fig. 1. Dispositif d'extraction: 1,4, robinets à 3 voies; 2, 3,5, robinets à 2 voies; A: compartiment servant au remplissage; B: compartiment d'extraction proprement dit; C: poire pour mise sous pression de B; D: à la trompe à vide; E: capillaire servant à l'élimination du solvant organique; F: capillaire permettant de récupérer la solution aqueuse.

*Mode opératoire.* La solution et le solvant sont introduits dans la partie A. En aspirant la solution dans B par la trompe à vide, l'air fait office d'agitateur en barbotant à travers la solution aqueuse et le solvant. Après quelques minutes, on ferme le robinet 2, coupe le vide et relie B à C au moyen du robinet 4. On met alors B sous pression au moyen de la poire C et en ouvrant 2, la solution aqueuse passe en A. Lorsque la surface de séparation des deux couches atteint l'extrémité effilée du capillaire E, on referme 2. En ouvrant 3 et en maintenant la pression dans B, le solvant est éliminé par le capillaire E. On introduit en A une nouvelle quantité de solvant et on recommence l'extraction comme ci-dessus. L'opération est terminée lorsque la solution aqueuse est incolore.

Après la dernière extraction, on fait couler la solution aqueuse par le capillaire F dans une ampoule à décanter. On lave A et B pour entraîner les dernières traces de Ni retenues aux parois. Ces eaux de lavages seront ajoutées à la solution aqueuse. L'appareil est alors prêt pour une nouvelle séparation après rinçage avec de l'eau, de l'alcool et de l'éther.

*Remarques.* Si le capillaire reste vide, au début des opérations d'extraction, on remarque lors de la mise sous pression de B, une légère montée de la solution aqueuse dans ce capillaire. Il faut donc, avant de commencer une séparation, remplir le capillaire E de solvant afin d'empêcher ce phénomène. Pour éviter cette montée au cours des extractions, il suffira de fermer le robinet 3 avant que l'air puisse s'introduire dans le capillaire. Les pertes en nickel au cours des extractions du cobalt sont faibles. Il a été effectué, sur des solutions de nickel à diverses concentrations, 5 extractions en utilisant pour chacune d'elles 10 ml d'acétate d'éthyle, puis le nickel restant dans la phase aqueuse a été dosé par la méthode de FERGUSON ET BANKS[2]. Les résultats sont rassemblés dans le Tableau V.

TABLEAU V

| *Ni théorique* µg | *Ni trouvé* µg | *Ni par ml* µg | *Erreur* % |
|---|---|---|---|
| 14.7 | 15.0 | 0.294 | +2 |
| 29.5 | 28.5 | 0.590 | —4 |
| 59.0 | 57.5 | 1.118 | —3 |
| 118.0 | 114.0 | 2.360 | —3 |
| 236.0 | 230.0 | 4.720 | —3 |
| 295.0 | 288.0 | 5.900 | —3 |

Bien que nous nous soyons placés dans les plus mauvaises conditions, les pertes restent légères; les 5 extractions ne sont nécessaires que si les quantités de cobalt sont considérables. Dans le Tableau suivant nous indiquons le nombre d'extractions qu'il faut faire selon la quantité de cobalt en solution.

TABLEAU VI

| *Co à extraire* mg | *Nombre d'extractions* | *Solvant utilisé* ml |
|---|---|---|
| 700 | 5 | 50 |
| 300 | 4 | 40 |
| 125 | 3 | 30 |
| 25 | 2 | 20 |

L'extraction est gênée par les ions $Hg^{+2}$ et $Hg_2^{+2}$ même en faibles proportions et les ions $Pb^{+2}$ en grandes quantités.

### DOSAGE COLORIMÉTRIQUE DU NICKEL PAR LA NIOXIME

La nickel-nioxime est soluble dans la quinoléine et lui confère une coloration jaune dont le coefficient d'extinction moléculaire est suffisamment grand pour rendre possible un dosage colorimétrique. La quinoléine „Fluka puriss" utilisée a un point d'ébullition de 236–237°. Elle est incolore. Le premier objet de cette mise au point a été d'étudier le comportement de ce solvant au spectrophotomètre.

#### *Spectre d'absorption de la quinoléine*

Nous avons constaté que celui-ci varie, pour la substance anhydre, avec le degré d'oxydation. Il dépend aussi de la quantité d'eau que renferme la quinoléine, la Fig. 2 met ce phénomène en évidence.

Pour obtenir la courbe B, nous avons introduit dans la cuve de comparaison de la quinoléine saturée d'eau bidistillée de pH 6. La littérature indique que cette substance saturée d'eau en renferme 22%, sans spécifier le pH. Avec l'eau bidistillée nous obte-

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nons le même résultat, par contre avec de l'eau tamponnée entre les pH 2 et 10, les solubilités observées ont toujours été trouvées plus faibles; effet de sel et de pH probablement.

Pour connaître l'influence de l'eau dissoute dans la quinoléine sur le coefficient d'extinction, nous avons déterminé la densité optique D, à deux longueurs d'onde, de la quinoléine en présence de quantités variables d'eau bidistillée, comparée à la quinoléine anhydre. Les résultats sont donnés dans le Tableau VII.

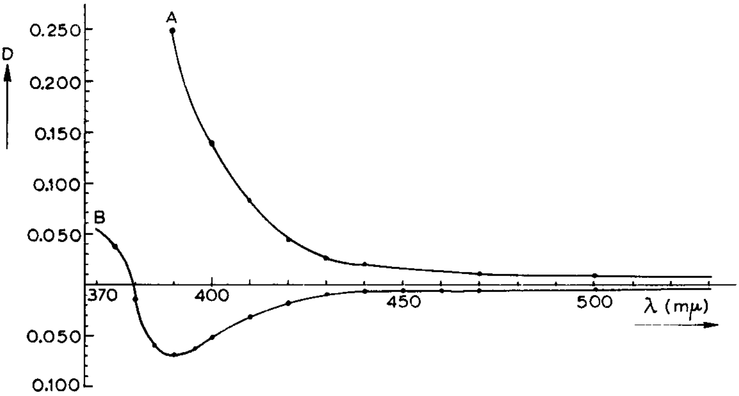

Fig. 2. Courbe A: spectre d'absorption de la quinoléine anhydre par rapport à l'eau bidistillée; Courbe B: spectre d'absorption de la quinoléine anhydre comparée à la quinoléine saturée en eau.

TABLEAU VII

| *Quinoléine anhydre (ml)* | *Eau ajoutée (% en vol)* | *D à 436 mμ* | *D à 405 mμ* |
|---|---|---|---|
| 5 | 5 | 0.005 | 0.035 |
| 5 | 10 | 0.006 | 0.042 |
| 5 | 20 | 0.003 | 0.056 |
| 5 | 22 | 0.004 | 0.056 |

On peut dire qu'à partir de 436 mμ et même un peu avant, la variation de la teneur en eau de la quinoléine ne modifie pas sensiblement la densité optique. Il n'en est pas de même pour des longueurs d'onde inférieures ou égales à 405 mμ.

### *Solubilité de la nickel-nioxime dans la quinoléine*

Nous avons étudié la stabilité et la solubilité de la nickel-nioxime dans la quinoléine selon le mode opératoire donné à la p. 450. Il a été préparé six solutions renfermant des quantités croissantes de nickel dont la composition exacte est donnée ci-dessous.

La coloration s'intensifie avec la concentration en nickel. La solution VI se trouble immédiatement, la solution V le fait après 10 à 15 min, les solutions IV et III sont stables et limpides pendant 12 h seulement alors que les solutions I et II sont encore optiquement vides après trois jours. D'après les densités optiques et la courbe d'éta-

TABLEAU VIII

| *Essai No* | *I* | *II* | *III* | *IV* | *V* | *VI* |
|---|---|---|---|---|---|---|
| *Phase aqueuse* | | | | | | |
| Tampon pH 5 (ml) | 2.475 | 2.45 | 2.4 | 2.3 | 2.1 | 2.0 |
| Nioxime 0.01*M* (ml) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| $NiCl_2$ 0.0078*M* (ml) | 0.025 | 0.050 | 0.1 | 0.2 | 0.4 | 0.5 |
| *Phase organique* | | | | | | |
| Quinoléine (ml) | 2 | 2 | 2 | 2 | 2 | 2 |
| *Conc. en Ni* (µg/ml)<br>dans 5 ml de solvant | 2.28 | 4.57 | 9.13 | 18.27 | 36.53 | 45.7 |
| Après 10 min | 0.060 | 0.115 | 0.225 | 0.430 | 0.855 | — |
| Après 3 jours | 0.065 | 0.110 | 0.125 | 0.115 | 0.130 | — |

lonnage, il a été possible d'évaluer la solubilité de la nickel-nioxime dans la quinoléine, elle est de 5 µg/ml après 3 jours et d'environ 18 µg/ml, 12 h après la mise en solution. Immédiatement après la préparation, elle est supérieure à 35/µg ml.

*Spectre d'absorption de la Ni-nioxime dans la quinoléine*

Les solutions sont préparées selon le mode opératoire décrit à la p. 450, 451, ce qui permet aussi d'apprécier la reproductibilité. Nous avons effectué pour chaque point 7 mesures de la densité optique dont nous donnons les valeurs extrêmes dans les colonnes 4 et 5 et la valeur moyenne dans la 2ième colonne du Tableau IX.

TABLEAU IX

| $\lambda$ (*mµ*) | *D* | $\varepsilon$ | *D max* | *D min* |
|---|---|---|---|---|
| 370 | 0.255 | 3100 | 0.280 | 0.230 |
| 380 | 0.262 | 3300 | 0.275 | 0.250 |
| 385 | 0.268 | 3400 | — | — |
| 390 | 0.263 | 3200 | 0.266 | 0.260 |
| 400 | 0.205 | 2500 | 0.207 | 0.204 |
| 405 | 0.166 | 2100 | — | — |
| 410 | 0.146 | 1800 | 0.149 | 0.143 |
| 420 | 0.117 | 1500 | 0.121 | 0.114 |
| 430 | 0.112 | 1400 | 0.113 | 0.111 |
| 435 | 0.114 | 1400 | 0.114 | 0.113 |
| 440 | 0.115 | 1400 | 0.116 | 0.114 |
| 445 | 0.116 | 1400 | 0.116 | 0.115 |
| 450 | 0.105 | 1300 | 0.106 | 0.104 |
| 460 | 0.078 | 1000 | 0.078 | 0.077 |
| 470 | 0.056 | 700 | 0.056 | 0.056 |

On peut en conclure qu'au-dessous de 430 mµ les mesures ne sont pas reproductibles. Dès que $\lambda \geqslant 430$ mµ (depuis 425 mµ même) les erreurs ne dépassent pas 2%.

*Courbe d'étalonnage et dosage du nickel*

*Solutions utilisées.* Chlorure de nickel 0.0078*M*, nioxime 0.01*M*, solution tampon pH 5 (acide acétique $0.055N$ + acétate de sodium $0.141M$) quinoléine saturée en eau bidistillée.

*Appareil.* Photomètre Eppendorf, filtre 436 mµ.

*Mode opératoire.* On prélève, avec une micropipette de 0.2 ml, la quantité nécessaire de la solution de nickel, on l'introduit dans un tube à centrifuger de 10 ml avec 1 ml de tampon et un excès de nioxime. Après formation du précipité on ajoute 2 ml de quinoléine saturée d'eau bidistillée, on secoue pour former l'émulsion, la nickel-nioxime passe dans le solvant organique (cette opération est accélérée si on porte le mélange à env. 80°). Après refroidissement, on centrifuge et on sépare les phases. La solution de quinoléine est introduite dans un ballon jaugé de 5 ml, on complète avec une solution de quinoléine (solution utilisée préablalement pour le lavage du tube à centrifuger), puis on détermine la densité optique. Résultats: Tableau X et Fig. 4.

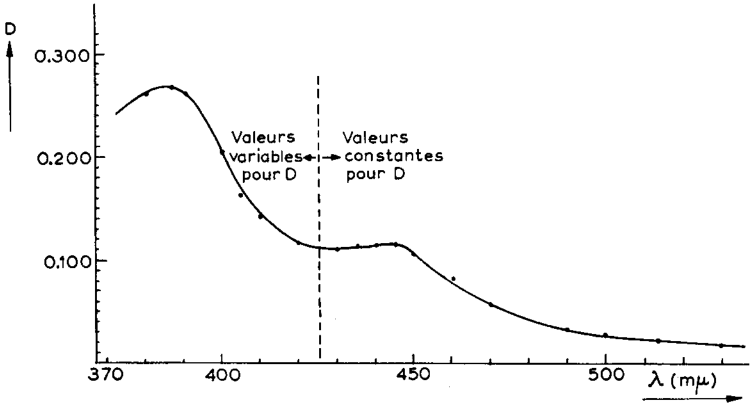

Fig. 3. Spectre d'absorption de la Ni-nioxime dissoute dans la quinoléine saturée en eau.

TABLEAU X

| $NiCl_2$ ml | Nioxime ml | Conc. Ni M | Conc. Ni µg/ml | D* | ε |
|---|---|---|---|---|---|
| 0.0125 | 0.100 | $0.194 \cdot 10^{-4}$ | 1.14 | 0.030 | — |
| 0.0250 | 0.100 | $0.368 \cdot 10^{-4}$ | 2.28 | 0.060 | — |
| 0.0500 | 0.200 | $0.760 \cdot 10^{-4}$ | 4.57 | 0.115 | — |
| 0.1000 | 0.300 | $1.552 \cdot 10^{-4}$ | 9.13 | 0.225 | 1440 |
| 0.1500 | 0.500 | $2.328 \cdot 10^{-4}$ | 13.70 | 0.340 | 1460 |
| 0.2000 | 0.600 | $3.104 \cdot 10^{-4}$ | 18.27 | 0.430 | 1390 |
| 0.2500 | 0.800 | $3.880 \cdot 10^{-4}$ | 22.84 | 0.530 | 1380 |
| 0.3000 | 0.900 | $4.656 \cdot 10^{-4}$ | 27.40 | 0.645 | 1390 |
| 0.4000 | 1.200 | $6.208 \cdot 10^{-4}$ | 36.53 | 0.855 | 1380 |

* Volume total de chaque solution: 5 ml.

Le coefficient d'extinction molaire est de $\varepsilon = 1420$, la coloration obéit à la loi de Beer. Il est encore possible de doser 2 µg de nickel par ml et jusqu'à 35 µg. Le photomètre Eppendorf permettant d'apprécier une variation de densité optique de 0.003, la sensibilité de la méthode est de 0.12 µg. On fait donc une erreur de 6%, erreur d'appareillage lorsqu'on dose 2 μg de nickel par ml. Dans le Tableau XI, nous comparons notre méthode à l'excellente méthode proposée par FERGUSON ET BANKS.

La méthode de FERGUSON ET BANKS est aussi précise que la nôtre et quatre fois plus sensible. Elle est quelque peu gênée par les variations de pH ou en présence de fortes concentrations d'électrolytes ce qui n'est pas le cas pour notre procédé. Elle est plus limitée aussi en ce qui concerne les limites de concentrations entre lesquelles le dosage est possible.

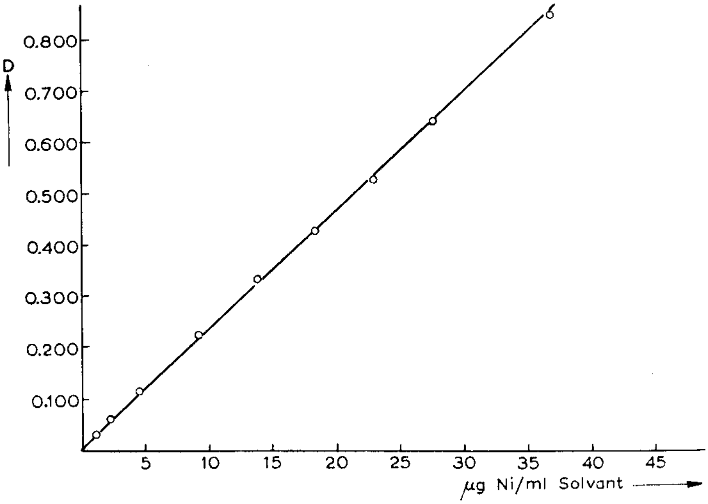

Fig. 4. Courbe d'étalonnage de la Ni-nioxime en solution dans la quinoléine saturée en eau. Cuve de comparaison: quinoléine saturée en eau; longueur d'onde: 436 mμ; longueur de la cuve: 1 cm; Concentration de la solution de base: 0.0078*N*.

TABLEAU XI

COMPARAISON DES DEUX MÉTHODES

| *Caractéristiques* | *Solution dans quinoléine* | *Suspension* |
|---|---|---|
| Limite inférieure : | 2 μg/ml | 0.5 μg/ml |
| Limite supérieure : | 35 μg/ml | 8.0 μg/ml |
| Temps de stabilisation : | 10 min | 30 min |
| Influence con. électrol. : | aucune | légère |
| Influence du pH : | aucune | légère |
| $\varepsilon$ moyen : | 1412 | 5600 |

## APPLICATIONS

### 1. *Dosage du nickel dans les sels de cobalt*

Comme nous l'avons vu, l'extraction directe de la nickel-nioxime, précipitée dans une solution aqueuse, par le benzène exige, s'il y a un grand excès de cobalt une trop grande quantité de réactif et la séparation n'est pas toujours quantitative. Nous proposons donc d'effectuer une préextraction au thiocyanate, comme il a été décrit dans la première partie. Nous préférons ce processus à celui préconisé par JOHNSON

*Bibliographie p. 455*

ET SIMMON[4], qui se basent sur une réaction proposée par FEIGL[5]. Le cobalt est oxydé en cobalti cyanure par un courant d'air, en présence d'ions cyanogène. Le complexe obtenu avec le nickel est détruit par le formaldéhyde alors que le complexe du cobalt subsiste. Ces auteurs séparent 1 partie de nickel dans 10.000 de cobalt avec une erreur de —7%. La méthode est bonne mais l'emploi du cyanure présente des inconvénients et la durée du dosage est de deux heures environ.

L'extraction au thiocyanate nous parait avantageuse, elle est plus rapide et plus effective. Pour ce faire nous utilisons les solutions suivantes: $NiCl_2$ $0.01M$, nioxime $0.0563M$, $NH_4SCN$ 60%, HCl conc. 36.4%, $NH_3$ 25%, HCl $5N$, $NH_3$ $5N$.

*Mode opératoire.* On dissout 0.2 à 0.7 g du sel de cobalt à doser dans 5 ml de HCl $5N$ directement dans le compartiment A du séparateur Fig. 1. On ajoute 10 ml de la solution $NH_4SCN$ qui fait apparaître la couleur bleue du thiocyanate de cobalt. On introduit 10 ml d'acétate d'éthyle et fait passer le tout dans le compartiment B Fig. 1. Lorsque le solvant a atteint sa couleur maximum on laisse décanter et sépare le solvant comme indiqué à la p. 447. On ajoute 0.1 ml HCl conc. puis une nouvelle quantité de solvant (10 ml). On vérifie au papier indicateur le pH qui doit être inférieur à 2 et on recommence l'opération jusqu'à ce que l'acétate d'éthyle ne présente plus de coloration. La dernière extraction terminée, on reçoit dans une ampoule à décanter la solution aqueuse qui s'écoule par F. On lave A et B du séparateur par 3 ml de $NH_3$ $5N$, puis 2 ml d'eau distillée. Le pH est porté à une valeur comprise entre 5 et 10

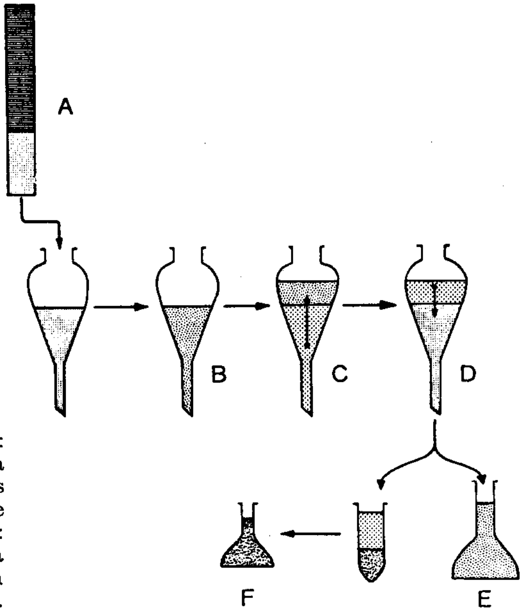

Fig. 5. Schéma de la séparation du cobalt: A: séparateur; B: précipitation du Ni par la nioxime; C: passage de la Ni-nioxime dans le benzène; D: dissociation de la Ni-nioxime et passage du Ni en solution aqueuse; E: dosage du Ni par mise en suspension de la Ni-nioxime; F: dosage du Ni par mise en solution de la Ni-nioxime dans la quinoléine.

▥ Solution aqueuse contenant le $Ni^{+2}$;

▒ Phase contenant les ions autres que le $Ni^{+2}$;

▩ Phase contenant la Ni-nioxime en suspension;

■ Solution organique contenant le cobalt;

▦ Quinoléine + Ni-nioxime en solution.

*Bibliographie p. 455*

par addition de $NH_3$ $5N$, puis on précipite le nickel par 5 ml de nioxime $0.0563M$. Après 10 minutes, la Ni-nioxime renfermée dans l'ampoule à décanter est séparée des dernières traces de cobalt au moyen du benzène (10 ml). On agite pour provoquer l'émulsion. La Ni-nioxime passe dans la phase organique. On sépare les deux liquides, élimine la solution aqueuse, lave le benzène trois fois avec 5 ml de $NH_3$ $5N$ et deux fois avec 5 ml d'eau bidistillée. La dernière portion de $NH_3$ doit être incolore. Le nickel passe en solution aqueuse lorsqu'on ajoute 5 ml de la solution HCl $5N$. Après agitation, on laisse décanter puis on reçoit la solution chlorhydrique dans un ballon jaugé de 50 ml. On lave deux fois le solvant avec 5 ml d'eau pour récupérer les dernières traces de nickel retenues par le benzène et les parois de l'ampoule, puis on dose le nickel par une des deux méthodes citées. Dans le cas présent, celle de FERGUSON ET BANKS est plus rapide que la nôtre, aussi l'avons nous utilisée.

Les dosages ont été effectués sur le chlorure de cobalt et sur le nitrate de cobalt de la maison Merck. Les résultats sont donnés dans le Tableau XII et le schéma du processus d'extraction dans la Fig. 5.

TABLEAU XII

| *$CoCl_2 \cdot 6\ H_2O$ Merck „Nickelfrei" Lot. No 84.327 Prise 1.0 g* | | | | | |
|---|---|---|---|---|---|
| *Ni ajouté* µg | *Ni total trouvé* µg | *Ni dans le sel* µg | *Rapport* Ni/Co | *Ni dans le sel* % | *Erreur* % |
| 118 | 238 | 120 | 1/1050 | 0.0120 | ±2.5 |
| 59 | 178 | 119 | 1/1400 | 0.0119 | ±2.0 |
| 0 | 116 | 116 | 1/2000 | 0.0116 | ±1.5 |
| *$Co(NO_3)_2 \cdot 6\ H_2O$ Merck garantie $Ni < 0.001\%$ Lot No 321.913 Prise 3.4 g* | | | | | |
| 0 | 23 | 23 | 1/30.000 | 0.00068 | ±2.5 |
| 59 | 84 | 35 | 1/8215 | 0.00073 | ±3.0 |
| 118 | 142 | 24 | 1/4155 | 0.00070 | ±2.0 |

Les erreurs ont été calculées en tenant compte des valeurs extrêmes trouvées pour le nickel total sur une série de 6 dosages.

### 2. *Séparation et dosage du nickel dans un mélange de plusieurs cations*

Pour mettre à l'épreuve la sélectivité de notre méthode d'extraction, nous avons effectué le dosage du nickel en présence d'importantes quantités de $Cu^{+2}$, $Al^{+3}$, $Fe^{+3}$ et $Ca^{+2}$. La solution renferme 1 mg/ml des sels suivants: $CuCl_2$, $Al(NO_3)_3$, $Fe(NO_3)_3$ et $CaCO_3$. Ils ont été dissous dans l'acide chlorhydrique $5N$. Comme les substances utilisées pro anal renferment des traces de nickel, nous avons fait le dosage du nickel sur ce mélange, pour obtenir le blanc, puis des quantités variables de nickel ont été ajoutées et le nickel total dosé. Les résultats sont donnés dans le Tableau XIII. Il a été procédé de la façon suivante: Des essais préliminaires ont montré que, même dans ce cas, une préextraction au thiocyanate est à recommander. On élimine ainsi la plus grande partie des ions gênants. La solution est introduite dans le compartiment A (Fig. 1) du séparateur et on procède comme il a été dit à la p. 453, seul change le pH auquel on effectue la séparation au moyen du benzène. En effet, après l'extraction au thiocyanate, on porte la solution au pH 3.5 par addition de NaOH $N$ (papier indicateur), lave les compartiments A et B avec une solution tampon pH 3.5 (acide acétique 0.185$N$ + acétate de sodium 0.015$M$). Le benzène est lavé une première fois avec 5 ml de la solution tampon puis 2 fois avec 5 ml de $NH_3$ $N$ et une dernière fois au moyen de 5 ml d'eau distillée. Le nickel est dosé selon la méthode décrite à la p. 448. Les résultats des dosages sont donnés ci-dessous.

TABLEAU XIII

| *Ni dans 5 ml de solution de base µg* | *Ni ajouté µg* | *Ni total µg trouvé* | *Ni ajouté trouvé µg* |
|---|---|---|---|
| 13.5 | 59.0 | 75 | 61.5 |
| 12.8 | 88.5 | 102 | 89.2 |
| 13.2 | 59.0 | 72 | 58.8 |

## CONCLUSIONS

La méthode de séparation préconisée est satisfaisante et présente une bonne sélectivité, elle permet de doser quelques gammas de nickel en présence de grandes quantités de la plupart des cations et avec une bonne précision. Le temps pour effectuer deux dosages est d'une heure environ. On trouvera plus de détails sur ce travail dans la thèse de W. HAERDI[6].

## RÉSUMÉ

La méthode de séparation proposée permet de doser le nickel en présence d'une grande quantité d'ions étrangers. Elle consiste à extraire la nickel-nioxime précipitée en solution aqueuse par le benzène. Celle-ci passe quantitativement dans ce dernier sans se dissoudre. Après élimination de l'eau, le benzène est repris par une solution chlorhydrique, dans laquelle la nickel-nioxime se dissout. On peut ainsi séparer le nickel d'un grand nombre de cations. Cependant, s'ils sont en trop grande proportion, il est préférable d'effectuer une préextraction au thiocyanate, dans l'acétate d'éthyle. Il a aussi été établi une méthode de dosage du nickel par la nioxime en dissolvant le complexe dans la quinoléine, ce qui permet de doser de 2 à 35 µg de nickel. Nous avons appliqué cette méthode de séparation à la détermination du nickel dans les sels de cobalt Merck (chlorure et nitrate) et nous avons montré que ce dosage était encore possible pour 1 partie de nickel dans 30.000 de cobalt.

## SUMMARY

A method is described for the separation and determination of µg-quantities of nickel in the presence of large quantities of foreign cations, by extracting nickel-nioxime with organic solvents.

## ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Trennung und Bestimmung von µg-Mengen Nickel neben grossen Mengen anderer Kationen durch Extraktion von Nickel-nioxim mit organischen Lösungsmittel.

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# SUB-MICROGRAM-SCALE ANALYSIS BY COULOMETRY AT CONTROLLED POTENTIAL

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## INTRODUCTION

The utility of coulometry at controlled potential in analyses at the decigram to milligram level is now well established, but the practical problems involved in securing accurate current integrations at that level have been solved too recently to permit any concern with the further problems that may be expected to arise in dealing with much smaller amounts of material. Meanwhile many successful applications of coulometry at controlled current to microgram-scale analyses have been described. These facts have led to a general belief that the controlled-current technique is the more useful of the two in trace analyses.

This belief has been held despite the demonstration by LORD, O'NEILL, AND ROGERS[1] that even millimicrogram amounts of silver can be determined with good accuracy by a procedure which, though quite different in apparatus and methodology, conforms to any operational definition of coulometry at controlled potential. More recently, using more conventional procedures, BOOMAN, HOLBROOK, AND REIN[2] have succeeded in determining 7.5 μg of uranium with a standard deviation of ± 2.2%, while MEITES[3] was able to obtain a mean deviation of ± 1.0% in the determination of 5.2 μg of chromium.

The present paper describes the results of an attempt to extend coulometry at controlled potential to its extreme lower limit, using a chemical system which was believed to be ideally suited to that purpose together with conventional apparatus and techniques for current integration. This attempt was made, partly in pursuance of the considerations described above, and partly in the hope of casting new light on the sources of error which afflict all analyses by coulometry at controlled potential and on the techniques by which these errors can be eliminated.

## EXPERIMENTAL

The Analytical Instruments, Inc. (Bristol, Conn.) potentiostat and electromechanical current integrator employed have been described elsewhere[4]. All electrolyses were carried out in a double-diaphragm cell[4], using a well-stirred mercury pool working electrode having an area of 47 cm$^2$, a commercial fiber-type saturated calomel reference electrode, and a helical platinum wire auxiliary electrode. A few drops of saturated hydrazine dihydrochloride were added to the supporting electrolyte solution in the auxiliary electrode compartment of the cell to prevent anodic attack of the platinum. A 1.5-V dry cell in series with the auxiliary electrode was used to permit the potentiostat to maintain control throughout each electrolysis in which the working electrode was anodic[3]. Where necessary, a decade resistance box in series with the bias battery was employed to limit the initial current to a value just smaller than the rated maximum value for the integrator input resistor employed. This unusual step was prompted by the extremely rapid decrease of the electrolysis current: had an input resistor been used which was small enough to bring about accurate integration of the initial current, too few counts would often have been secured to permit the maximum precision to be attained. Measurements of the electrolysis current were made with a multi-range milliammeter in the electrolysis circuit.

Oxygen was excluded from the working electrode compartment of the cell by a very rapid stream of prepurified nitrogen which had been passed through two efficient gas-washing bottles containing 0.1 $F$ chromous chloride, 1 $F$ hydrochloric acid, and excess heavily amalgamated zinc, then through a similar bottle containing water, and finally through still another bottle containing the ammoniacal supporting electrolyte used. The first and second of these bottles served to remove the trace of oxygen present in the nitrogen[3], the third to trap droplets of chromous chloride that might have been sprayed over, and the fourth to prevent excessive volatilization of ammonia from the solution being electrolyzed.

A stock 0.05$M$ solution of zinc ion in 0.2$F$ hydrochloric acid was prepared determinately from pure metallic zinc. More dilute zinc solutions were prepared from this by dilution with 0.2 $F$ hydrochloric acid, using carefully calibrated volumetric glassware. Other chemicals used were ordinary reagent grade.

"Vacumetal" mercury (Metalsalts Corp., Hawthorne, N. J.) was used without further purification in all determination involving as much as 0.5 mg of zinc, but the ammonia and ammonium monohydrogen citrate used to prepare the supporting electrolyte contained enough zinc to cause a detectable error even at the 5-mg level. Hence the supporting electrolyte was usually freed from zinc immediately before use by an electrolysis at —1.50 V *vs.* S.C.E.; the zinc amalgam formed in this step was drained out of the cell and replaced by fresh mercury before the actual analysis was commenced. For determinations of less than 0.5 mg of zinc, mercury was used which had been previously purified by anodic stripping into purified ammoniacal citrate at —0.50 V *vs.* S.C.E.

## DATA AND DISCUSSION

The sensitivity of coulometry at controlled potential is ultimately limited by the magnitude of the correction that must be made for the background quantity of electricity, *i.e.*, the quantity of electricity which is consumed at the working electrode by processes other than the one of interest. Five components of this background quantity of electricity have been distinguished by MEITES AND MOROS[5], but only three are relevant to the determination of zinc by the present method. These are the "charging" or "condenser" quantity of electricity, $Q_c$, required to charge the working electrode and the electrical double layer at its surface up to the control potential; the "faradaic impurity" quantity of electricity, $Q_{f,i}$, required to oxidize or reduce impurities in the mercury and the supporting electrolyte; and the "continuous faradaic" quantity of electricity, $Q_{f,c}$, which results from the reduction of hydrogen ion, water, ammonium ion, or some other constituent of the supporting electrolyte whose concentration remains substantially unchanged throughout the electrolysis.

When the working electrode area is about 50 cm$^2$, as was the case in this investigation, $Q_c$ could hardly exceed 10 m$\mu$ F$_y$, as pointed out by MEITES AND MOROS. It is therefore significant only at or below the microgram level. The value of $Q_{f,i}$ has no such natural limit, but it can be made negligibly small by appropriate preliminary purification of the mercury and the supporting electrolyte. When this is done, $Q_c$ can be measured directly by the procedure illustrated by Fig. 1(a). To minimize difficulties that might otherwise be caused by traces of surface-active materials which affect the capacity of the double layer, it is preferable to determine $Q_c$ immediately before the addition of the sample, using the same mercury and supporting electrolyte that will be used in the later analysis. The values of $Q_c$ thus obtained differ appreciably from one run to the next, but the fact that an absolute error of $\pm$ 0.2 m$\mu$-equiv. could be achieved in the determination of zinc indicates that each individual value of $Q_c$ is probably meaningful to within a few %.

Whereas $Q_c$ is essentially completely accumulated within a second or two after the start of the electrolysis*[5,6] and $Q_{f,t}$ approaches a constant value in accordance with LINGANE's equation[7], $Q_{f,c}$ increases linearly with time and thus represents an error which increases virtually indefinitely as the electrolysis is prolonged. This error can, it is true, be eliminated by making periodic measurements of $Q_{total}$, the total quantity of electricity accumulated, at times so long that the desired working electrode reaction is complete, and extrapolating $Q_{total}$ to zero time. An example of this procedure was given by MEITES AND MOROS[5]. In practice, however, the uncertainty introduced by this extrapolation becomes intolerably large on the submicrogram scale unless the continuous faradaic current is very small or the extrapolation very short.

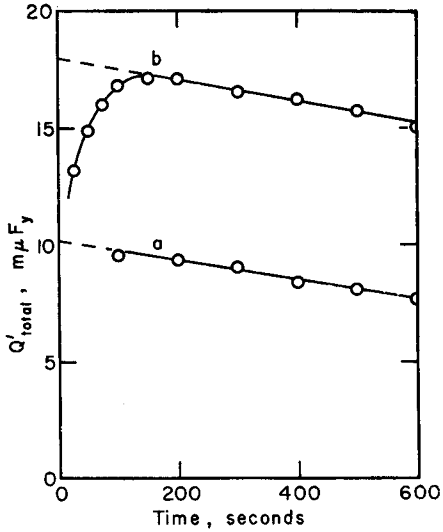

Fig. 1. Variation of $Q'_{total}$ with electrolysis time during typical electrolyses of (a) 65 ml of electrolytically purified 2 $F$ ammonia–1 $F$ ammonium citrate with 25 ml of electrolytically purified Hg, and (b) same + 0.007802 μequiv. (0.255 γ) of zinc. The data were secured at —0.50 V *vs.* S.C.E. immediately after an electrolysis at —1.40 V *vs.* S.C.E.

From these considerations it is obvious that the best sensitivity and accuracy will be secured when the final current integration is performed during an electrolysis which proceeds very rapidly and which involves only a very small continuous faradaic current.

The first of these desiderata is rather difficult to achieve when the substance being determined is initially in the solution phase. This is because the rate of the electrolysis then depends, according to LINGANE's equation[7], on the diffusion coefficient of the ion or molecule being reduced, on the ratio of electrode area to solution volume, and on the thickness of the Nernst diffusion layer. By using a large efficiently stirred working electrode and the minimum possible volume of solution, it is generally possible to achieve 99.9% completion in about 15 min. But a further substantial increase

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* This is not true when the initial current is limited by the insertion of a series resistor into the electrolysis circuit, as was sometimes done in this work, because the working electrode potential then drifts with time up to the control potential, so that the accumulation of $Q_c$ becomes complete only when the electrolysis current begins to fall below the artificially imposed limit. This, however, has no effect on the final value of $Q_c$.

in this rate can be effected only by increasing the diffusion coefficient of the species being determined.

This could be done by raising the temperature, but this approach is neither practical nor useful. Taking the ordinary temperature coefficient of the diffusion coefficient as +2% per degree, increasing the temperature from 25° to 95° during an electrolysis would barely quadruple the electrolysis rate. To be sure, this might be a profitable approach for the routine analytical laboratory which is desirous of obtaining the greatest possible use from its instrument. On the other hand, it is useless in submicrogram analysis, because $i_{f,c}$ increases with increasing temperature, and in the extrapolation to zero time this introduces an increased uncertainty which more than counterbalances the advantage derived from increasing the rate of the electrolysis.

In the present work, advantage was taken of the fact that the diffusion coefficient of a metal dissolved in mercury is often considerably larger than that of a metal ion in aqueous solution[8]. Thus, from LINGANE's data on the polarographic diffusion current constant of zinc(II) in ammoniacal ammonium chloride[9], the diffusion coefficient of this ion at 25° is calculated from the Ilkovic equation to be $9.9 \cdot 10^{-6}$ cm²/sec. The diffusion coefficient of zinc in mercury has been measured by MEYER[10], VON WOGAU[11], WEISCHEDEL[12], and FURMAN AND COOPER[13]; from the concordant results of WEISCHEDEL and FURMAN AND COOPER, one estimates that in very dilute amalgams the diffusion coefficient of zinc is approximately $1.7 \cdot 10^{-5}$ cm²/sec. Therefore the anodic stripping of zinc should proceed almost twice as rapidly as the cathodic deposition of zinc ion if the volumes of solution and mercury are identical and if the Nernst diffusion layer thicknesses are the same for the anodic and cathodic processes. In fact, however, it is easy to carry out an electrolysis with only one-half to one-fourth as much mercury as solution, and in addition it appears that the Nernst diffusion layer thickness for the anodic process is appreciably smaller than for the cathodic process. The actual rates of these two processes in a typical experiment are indicated by Fig. 2, which shows that the stripping is 99.9% complete within about 3 min.

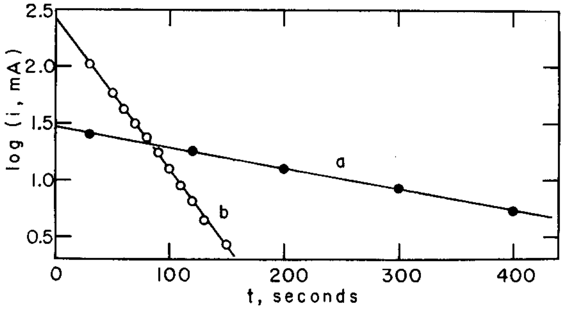

Fig. 2. Current–time curves obtained for (a) the reduction of 80 μequiv. of zinc from 50 ml of 2 *F* ammonia–1 *F* ammonium citrate at −1.45 V *vs.* S.C.E., and for (b) the subsequent reoxidation of the same quantity of zinc from the 25-ml amalgam electrode at −0.70 V *vs.* S.C.E.

The extreme rapidity of the stripping process permits the correction for $i_{f,c}$ to be made by means of a very short extrapolation, and in addition it is a simple matter to carry out the stripping at a potential where $i_{f,c}$ is very small. As was pointed out above, these conditions are essential to the success of controlled-potential coulometric analyses on the submicrogram level.

An ammoniacal ammonium citrate supporting electrolyte was selected for this work on the basis of polarographic data secured by KARP AND MEITES[14,15], which indicated that such a medium should be well suited to the determination of zinc in the presence of other elements commonly encountered in non-ferrous alloys. A "2 *F* ammonia–1 *F* ammonium citrate" solution (3 moles of ammonia and one mole of diammonium hydrogen citrate per liter) was used to minimize the cell resistance and to enable substantial concentrations of metal ions to be handled. Fig. 3 shows typical current–potential curves of zinc(II) and zinc amalgam in this medium. From these curves it is apparent that zinc(II) can be quantitatively reduced at any potential more negative than about —1.35 V *vs.* S.C.E., and that zinc can be quantitatively stripped out of the amalgam at any potential more positive than about —1.20 V *vs.* S.C.E. To avoid any formation of ammonium amalgam, which would lead to a high and erratic consumption of electricity in the stripping step, it is preferable to carry out the deposition at —1.40 or —1.45 V *vs.* S.C.E. In dealing with substantial amounts (0.1 mg or more) of zinc, good results can be secured by carrying out the stripping at —1.00 V even if the continuous faradaic current is neglected. However, the correction for $i_{f,c}$ at such negative potentials becomes undesirably large when smaller quantities of zinc are involved, and hence for maximum sensitivity it is preferable to carry out the reoxidation at about —0.50 V.

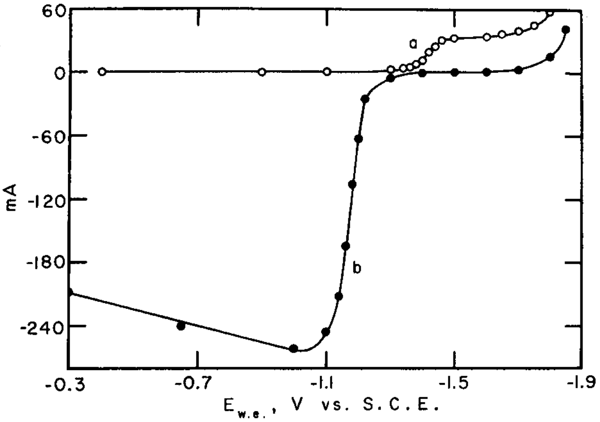

Fig. 3. Current–potential curves for (a) 0.6 m*M* zinc (II) in 2 *F* ammonia–1 *F* ammonium citrate, and (b) the amalgam electrode prepared by the quantitative reduction of 50 ml of the solution of curve *a* with 25 ml of mercury at —1.45 V *vs.* S.C.E.

Attention may be called to the fact that the amalgam electrode at the completion of the deposition step is at a potential where $i_{f,c}$ is by no means negligible. If the amalgam is then allowed to stand with the electrolysis current off, the zinc will reenter the solution at a rate which is proportional to this value of $i_{f,c}$. Especially when dealing with small amounts of zinc, therefore, it is essential to begin the stripping as rapidly as possible after the reduction is completed.

TABLE I

COULOMETRIC DETERMINATION OF ZINC

| *Microequivalents Zn taken* | | *Number of determinations* | *Average microfaradays consumed* | | *Error of mean, %* |
|---|---|---|---|---|---|
| 1986.8 | (65 mg) | 4 | 1988.6 | ± 0.11% | + 0.09 |
| 991.2 | | 3 | 991.6 | ± 0.11% | + 0.04 |
| 398.1 | | 4 | 397.7 | ± 0.07% | — 0.10 |
| 159.85 | | 2 | $159.8_7$ | ± 0.03% | + 0.01 |
| 59.28 | | 2 | 59.27 | ± 0.02% | — 0.02 |
| $19.75_2$ | | 3 | 19.734 | ± 0.07% | — 0.09 |
| 7.857 | | 2 | 7.858 | ± 0 00% | + 0.01 |
| $2.368_9$ | | 3 | $2.370_0$ | ± 0.04% | + 0.05 |
| 0.7857 | | 2 | 0.7852 | ± 0.05% | — 0.06 |
| 0.2352 | | 5 | 0.2356 | ± 0.14% | + 0.17 |
| 0.07791 | | 3 | 0.07724 | ± 0.34% | — 0.8 |
| 0.02346 | | 6 | 0.02359 | ± 0.5 % | + 0.4 |
| 0.007802 | | 4 | 0.00767 | ± 2.8 % | — 1.7 |
| 0.002298 | (0.07 μg) | 8 | 0.00219 | ± 10.3 % | — 5 |

Table I shows the results obtained when the method just described was applied to solutions containing known amounts of zinc. With quantities of zinc exceeding about 10 μg, an accuracy and precision of ± 0.1% are easily attainable. Even 1 μg of zinc can be determined with an accuracy and precision of ± 1% or better; this is comparable with what has been achieved by coulometric titrations under equally favorable conditions. As little as 0.07 μg of zinc can be determined with an accuracy and precision of about ± 10%, which corresponds to an uncertainty of about 0.2 mμ Fy.

This last value represents about 2% of the value of $Q_c$ under these conditions. It is therefore apparent that the ultimate sensitivity of controlled-potential coulometric analysis is governed primarily by the accuracy with which the necessary correction for $Q_c$ can be determined. A significant improvement in the relative error involved in this determination appears somewhat improbable, and hence it seems safe to say that the further extension of controlled-potential analysis into the millimicrogram range will be possible only if $Q_c$ can be reduced well below its value under these conditions. In principle this can be achieved in three ways. One is by considerably decreasing the area of the working electrode, which will cause a proportional decrease in the value of $Q_c$; this must be accompanied by a roughly proportional change of solution volume if electrolyses* are not to be unduly prolonged. This involves some difficulties, though by no means insuperable ones, in cell design. Another is to decrease the extent to which the working electrode potential is altered during the electrolysis: here this was 0.9 V, and this corresponds much more nearly to a maximum than to a minimum change. This, however, is not a truly general solution, for the potential change during any particular procedure is governed partly by the

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* Including, for example, the deposition step in the present procedure.

electrochemistry of the substance being determined and partly by the necessity of minimizing $i_{f,c}$ during the final electrolysis, and these are matters outside of the experimenter's control. A final possibility would involve adding to the solution a capillary-active substance whose adsorption at the electrode surface would lead to a considerable decrease of the double layer capacity.

## SUMMARY

The considerations which determine the success of controlled-potential coulometric analyses on the submicrogram level are discussed, and it is shown that the ultimate sensitivity of the method is governed by the accuracy with which the requisite background corrections, especially that for the charging quantity of electricity, can be determined. A method for the coulometric determination of zinc based on these considerations is shown to contain a limiting uncertainty of ± 0.2 mμFy, so that as little as 0.07 μg of zinc can be determined within about ± 10%, while quantities of zinc exceeding about 10 μg can be determined with an accuracy and precision of ± 0.1% or better. Possible techniques for the further extension of controlled-potential coulometric analysis into the millimicrogram range are briefly discussed.

## RÉSUMÉ

On examine les conditions d'application, à l'échelle ultramicrochimique, des analyses coulométriques à potentiel contrôlé. L'essai d'un dosage coulométrique de zinc montre qu'il est possible de déterminer jusqu'à 0.07 μg de cet élément avec environ ± 10% d'erreur, tandis que des quantités de zinc dépassant 10 μg peuvent être dosées avec une précision de ± 0.1% (ou même meilleure).

## ZUSAMMENFASSUNG

Es werden die Faktoren untersucht, welche die Ergebnisse coulometrischer Analysen mit kontrolliertem Potential bei Submikrogramm-mengen beeinflussen. Die coulometrische Bestimmung von Zink, unter Berücksichtigung dieser Faktoren, erlaubt Mengen bis zu 0.07 μg mit ca ± 10% Genauigkeit und Mengen von mehr als 10 μg mit ± 0.1% Abweichung zu erfassen.

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# COULOMETRIC TITRATION WITH ELECTROGENERATED +2 TIN

## DETERMINATION OF IODINE, BROMINE, AND VARIOUS OXIDANTS VIA IODOMETRY

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Although the roster of coulometric titrations now includes many reactions of classical titrimetry[1], the use of electrogenerated +2 tin as a coulometric titrant has not previously been reported. We have found that in an acidic bromide medium +4 tin (probably $SnBr_6^{-2}$) is reduced to the +2 state (probably $SnBr_4^{-2}$) with 100% current efficiency at a gold cathode. The formal potential of the stannic–stannous couple in bromide medium is +0.27 V *vs.* N.H.E., a value sufficiently reducing so that (in principle) +2 tin should serve for the titration of divers oxidants.

In practice one encounters the inconvenience that the rate of reduction of most substances by +2 tin is relatively small, but this can be circumvented by either of two means. Firstly, an excess of +2 tin can be generated in the test solution, and, after a short waiting period, the polarity of the generating electrode is reversed from cathode to anode and the excess +2 tin is titrated by the bromine electrogenerated at the anode. The other expedient, applicable to the determination of substances capable of oxidizing iodide to iodine, is "coulometric iodometry". An excess of iodide ion is added to the test solution, and the liberated iodine is titrated with the electrogenerated +2 tin. The iodine–stannous reaction is rapid, and equivalence points can be detected accurately either potentiometrically or amperometrically.

ROWLEY AND SWIFT[2] determined iodine (and thus various oxidants *via* iodometry) by adding a measured excess of standard thiosulfate solution, and back titration of the excess thiosulfate with electrogenerated iodine. This method suffers from the disadvantage of requiring a standard thiosulfate solution, and is only semi-coulometric. Derect titration of iodine with electrogenerated +2 tin is simpler and more convenient.

### EXPERIMENTAL

The coulometric titrations were performed in the usual manner[1]. The titration cell, whose capacity was *ca.* 175 ml, is shown in Fig. 1. The auxiliary electrode is separated from the titration chamber by two sintered glass disks, so that interchamber transfer is effectively minimized. The test solution was stirred efficiently with a magnetic stirrer.

Because oxygen is reduced concomitantly with +4 tin at the cathode, elimination of dissolved air from the solution is necessary. By using a non-oxygen producing auxiliary electrode (*e.g.* a cadmium rod in $0.5M$ cadmium chloride), and passing nitrogen through all of the chambers, oxygen was effectively excluded.

In most titrations of iodine, a gold generator cathode (1 × 1 cm) was employed. A platinum generator cathode (1 × 1 cm) was used in titrations of bromine, since bromine oxidizes gold in a bromide medium. Both bromine and iodine were generated at platinum anodes (1 × 1 cm).

The supporting electrolyte was $4M$ sodium bromide, $0.2M$ stannic chloride and $0.2N$ hydrochloric acid. The solution was first deaerated, and then made $0.01M$ in respect to potassium iodide when iodometric determinations were to be performed. The sample of the oxidant to be titrated was then added. Nitrogen was passed only over the surface of the solution during the titration to avoid volatilization of the bromine or iodine.

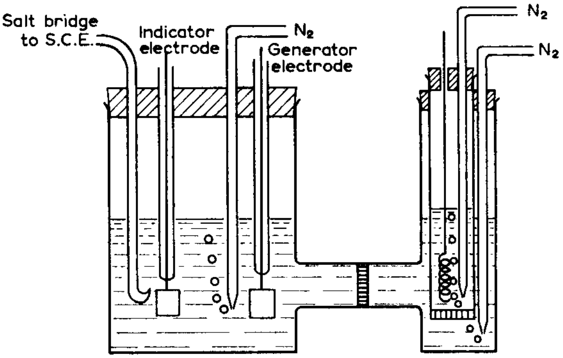

Fig. 1. Coulometric titration cell.

Potentiometric end-point detection with a platinum foil indicator electrode and saturated calomel reference electrode followed the usual practice. The amperometric detection system comprised two identical platinum electrodes (1 × 1 cm) across which 150 mV applied voltage was maintained. The indicator current was observed with a shunted galvanometer. Detailed discussions of both these end-point detection techniques as applied to coulometric titration are available in *Electroanalytical Chemistry*[1].

### *Current-efficiency for electrogeneration of +2 tin*

The electrogeneration of +2 tin was studied only in bromide and chloride media, because it is known from polarographic data that +4 tin produces well delineated reduction waves only in these media. Current efficiencies for the reduction of stannic ion in various chloride and bromide media at gold and platinum cathodes were estimated from current–potential curves with and without stannic ion present[1]. The same cell and conditions used for the coulometric titrations were employed.

These current–potential curves predicted current efficiencies closer to 100% with a gold cathode than with platinum, because gold has a higher hydrogen overvoltage. Although 100% current efficiency is not easily attainable in a chloride medium, a bromide medium (*ca.* $3M$) proved successful. The current efficiency is higher in bromide than in chloride medium because the bromostannate ion requires less overpotential for its reduction, and thus is reduced to the stannous state more in advance of hydrogen ion reduction, than the chloro-stannate ion.

A relatively large bromide ion concentration is necessary to maintain the major part of the +4 tin as $SnBr_6^{-2}$, and hydrogen ion also is essential to prevent its hydrolysis. With 0.2$M$ stannic tin the bromide ion concentration must be at least 2.8$M$, and 3 to 4$M$ is optimum. A range of hydrogen ion concentration from 0.15 to 0.4$M$ is satisfactory. At lower acidities hydrolysis of $SnBr_6^{-2}$ occurs, while at higher acidities hydrogen ion reduction concomitantly with reduction of $SnBr_6^{-2}$ becoms significant.

The supporting electrolyte finally selected as optimum was 4$M$ sodium bromide, 0.2$M$ stannic chloride, and 0.2$N$ hydrochloric acid. Bromide complexes stannic tin more strongly than chloride does, so the electrochemistry of this solution is characteristic of $SnBr_6^{-2}$.

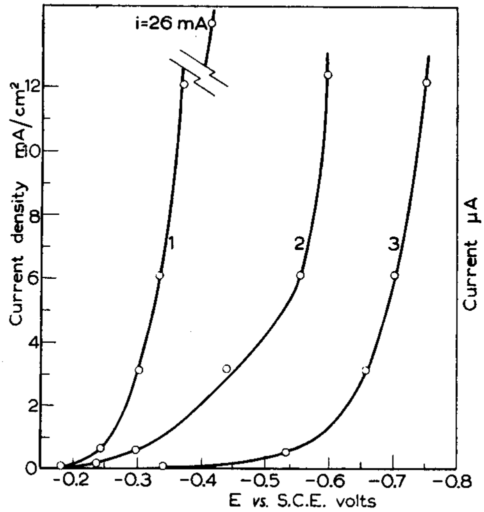

Fig. 2. Increase of hydrogen overpotential by tin oxide film on platinum cathode. In all cases the supporting electrolyte was air-free 3$M$ sodium bromide and 0.4$M$ perchloric acid, the area of the platinum cathode was 1.68 cm², and the solutions were stirred. (2) Supporting electrolyte alone with clean (unfilmed) platinum cathode. (3) Supporting electrolyte alone but cathode carried a film of hydrous stannic oxide. (1) 0.2$M$ stannic chloride present.

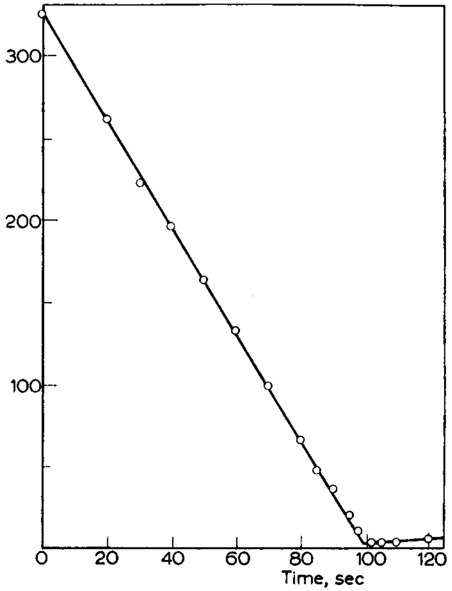

Fig. 3. Typical amperometric titration curve of 2.70 mg of iodine with electrogenerated +2 tin, using two 1 cm² platinum indicator electrodes subjected to an applied voltage of 150 mV.

With a *freshly cleaned* platinum cathode the current efficiency for reduction of $SnBr_6^{-2}$ is considerably short of 100%. However, once the platinum cathode has been used it functions nearly as efficiently as gold. During the reduction of the +4 tin the platinum cathode acquires a film of stannic hydrous oxide, which increases the hydrogen overpotential by about 150 mV and thus greatly minimizes co-reduction of hydrogen ion. This beneficial phenomenon is demonstrated by the current–potential curves in Fig. 2, and it will be discussed in detail in a separate communication. The film of stannic hydrous oxide is not removed by even prolonged washing with water, nor by gentle wiping with filter paper, so that no special care is needed in handling the filmed electrode. The film can be removed with hot hydrochloric or hydrobromic acids or sodium hydroxide.

The current efficiencies predicted from the current–potential curves were verified by direcly determining the amount of +2 tin produced under a particular set of conditions as follows. The +4 tin solution was electrolyzed at either a platinum or gold cathode with a known current for a measured time. The +2 tin produced was then back-titrated with electrogenerated iodine, employing an amperometric end-point as described in a following section. The average current efficiencies at current densities of 10 to 84 mA/cm$^2$ was for platinum 99.3 ± 0.2%, and for gold 99.7 ± 0.2%. With both electrodes the current efficiency decreased at current densities below 5 mA/cm$^2$.

TABLE I

COULOMETRIC TITRATION OF IODATE, IRON, AND CERIUM (IODOMETRICALLY) WITH ELECTROGENERATED STANNOUS ION

The solution was 4*M* sodium bromide, 0.2*N* hydrochloric acid, 0.008*M* potassium iodide, and 0.2*M* stannic chloride, with a volume of *ca.* 50 ml. A gold generator cathode (1 × 1 cm) was used, except as noted

| *Substance titrated* | *No. of trials* | *Current (mA)* | *Taken (mg)* | *Found (mg)* | *Mean deviation (mg)* | *Av. error %* | *End-point* |
|---|---|---|---|---|---|---|---|
| Iodate | 3 | 10.10 | 0.7174 | 0.7173 | 0.0007 | −0.05 | Amp. |
| | 3 | 22.78 | 1.794 | 1.795 | 0.001 | +0.02 | ,, |
| | 3 | 22.90 | 1.891 | 1.894 | 0.005 | +0.2 | ,, |
| | 3 | 22.89 | 1.891 | 1.892[a] | 0.005 | +0.1 | ,, |
| | 3 | 33.11 | 3.587 | 3.592 | 0.007 | +0.1 | ,, |
| | 1 | 22.98 | 1.891 | 1.897[b] | — | +0.3 | ,, |
| | 1 | 22.86 | 1.891 | 1.889[c] | — | −0.1 | ,, |
| | 5 | 10.10 | 0.3587 | 0.3595 | 0.0050 | +0.2 | Pot. |
| | 3 | 10.00 | 0.7174 | 0.7180 | 0.0021 | +0.05 | ,, |
| | 3 | 33.10 | 3.587 | 3.578 | 0.007 | −0.3 | ,, |
| Iron (+3) | 3 | 10.12 | 0.5640 | 0.5635 | 0.005 | −0.10 | Amp. |
| | 3 | 22.78 | 2.820 | 2.804 | 0.012 | −0.56 | ,, |
| | 3 | 33.14 | 5.640 | 5.635 | 0.011 | −0.10 | ,, |
| Cerium (+4) | 5 | 23.04 | 6.663 | 6.655 | 0.046 | −0.13 | ,, |
| | 2 | 33.26 | 13.33 | 13.38 | 0.01 | +0.35 | ,, |

[a] Platinum electrode 0.7 × 1.8 cm used.
[b] Solution made 0.06*M* in fluoride.
[c] Solution made 0.10*M* in fluoride.

### *Titration performance data*

*Coulometric iodometry.* Typical results of the iodometric determination of potassium iodate, +3 iron, and +4 cerium in Table I demonstrate that the titration is precise and accurate.

The shape of the amperometric titration curve is shown in Fig. 3. The current remains small after the end-point because the stannic–stannous couple behaves quite irreversibly, and the applied voltage of 150 mV is smaller than the total cathodic and anodic overpotentials.

Using potentiometric end-point detection, the equivalence point potential is +0.28 V *vs.* S.C.E. The supporting electrolyte was pre-titrated to this potential before the sample was added.

TABLE II

COULOMETRIC TITRATION OF BROMINE WITH +2 TIN

Bromine was produced *in situ* by addition of potassium bromate solution to *ca.* 50 ml of 4*M* sodium bromide, 0.2*M* stannic chloride, and 0.2*N* hydrochloric acid. The generator electrode was platinum, 0.8 × 2.0 cm.

| *Current (mA)* | *Potassium bromate (mg)* | | *% Error* |
|---|---|---|---|
| | *Taken* | *Found* | |
| 23.00 | 1.265 | 1.256 | —0.7 |
| | | 1.256 | —0.7 |
| | | 1.262 | —0.2 |
| | | 1.273 | 0.6 |
| | | 1.280 | 1.2 |
| | | 1.285 | 1.6 |
| | | 1.265 | 0.0 |
| | | 1.272 | 0.6 |
| | | 1.268 | 0.2 |
| | | Av. 1.269 ± 8 | 0.3 |
| 22.82 | 1.274 | 1.271 | —0.2 |
| | | 1.281 | 0.6 |
| | | 1.280 | 0.5 |
| | | Av. 1.277 ± 4 | 0.2 |
| 33.25 | 2.530 | 2.524 | —0.2 |
| 33.15 | 2.547 | 2.544 | —0.1 |
| | | 2.552 | 0.2 |
| | | 2.551 | 0.2 |
| | | Av. 2.549 ± 3 | 0.1 |
| 62.06 | 5.094 | 5.098 | 0.1 |

*Direct titration of bromine.* Typical results of the titration of bromine (generated *in situ* by the addition of potassium bromate) in Table II demonstrate that bromine may be determined with an average error of 0.2 to 0.3%. The amperometric end-point was similar to that obtained in the iodine titration.

The reaction tends to be slow near the end-point, but a titration can be completed in 5 min. When titrations were performed by successive additions of bromate samples to the supporting electrolyte, the first sample gave results about 0.001 milliequivalent low. Results with subsequent samples were close to the theoretical value. This negative error in the first titration was probably due to reducing impurities in the solution, and was eliminated by generating bromine at a platinum anode, stirring for 5 minutes, and titrating to the end-point with +2 tin, before the sample was added.

Titrations using potentiometric end-point detection were somewhat slower, since the bromine–bromide couple establishes potentials sluggishly at platinum electrodes.

### *Direct and reverse titrations with the stannous–bromine and stannous–iodine systems*

Because a bromide medium is used in generating +2 tin, the stannous–bromine couple (or by addition of a small amount of iodide, the stannous–iodine couple) can be employed *via* back titration in cases where direct titration is not feasible because of a too small reaction rate. By appropriate selection of polarity of the generator electrode in the test solution, bromine can be generated *via* anodic oxidation of bromide ion, or stannous tin can be generated by cathodic reduction of stannic ion. By generation of an excess of +2 tin and back-titration with either bromine or iodine, titration of dyes and other substances which are reduced only slowly by +2 tin is possible. Similarly +2 tin can be used as a back-titrant for slow oxidations, brominations or iodinations.

Typical results in Tables III and IV demonstrate that anodic and cathodic generation times coincide within a few parts per thousand at current densities of 5 to 84

TABLE III

DIRECT AND BACK TITRATIONS WITH THE STANNOUS—IODINE SYSTEM

The solution was 3.5*M* in sodium bromide, 0.2*M* in stannic chloride, 0.2*N* in hydrochloric acid, and 8 m*M* in potassium iodide. The volume was *ca.* 56 ml. The generator cathode was a gold electrode (1 × 1 cm), and the generator anode was of platinum (1 × 1 cm).

| *Current (mA)* | *Substance generated first* | *Iodine gener. time (sec)* | *Stannous gener. time (sec)* |
|---|---|---|---|
| | *Amperometric end-point* | | |
| 5.218 | iodine | 100.0 | 100.3 |
| | stannous | 99.1 | 100.0 |
| 9.975 | iodine | 100.0 | 100.3 |
| | stannous | 99.8 | 100.0 |
| 23.06 | iodine | 100.0 | 100.0 |
| | stannous | 99.4 | 100.1 |
| 41.08 | iodine | 100.0 | 100.1 |
| | stannous | 99.5 | 100.0 |
| 84.05 | iodine | 49.98 | 50.13 |
| | stannous | 49.86 | 49.93 |
| | *Potentiometric end-point* | | |
| 10.05 | iodine | 100.0 | 100.1 |
| | stannous | 99.7 | 100.0 |
| 20.54 | iodine | 100.0 | 100.0 |
| 31.34 | iodine | 100.0 | 99.9 |
| | stannous | 100.0 | 100.0 |
| 86.01 | iodine | 50.01 | 50.13 |
| | stannous | 49.92 | 50.00 |

TABLE IV

DIRECT AND BACK TITRATIONS WITH THE STANNOUS–BROMINE SYSTEM

The solution was 3.5$M$ sodium bromide, 0.2$M$ stannic chloride, and 0.2$N$ hydrochloric acid. The volume was *ca.* 57 ml. The generator electrode was platinum (1 × 1 cm).

| *Current (mA)* | *Substance generated first* | *Bromine gener. time (sec)* | *Stannous gener. time (sec)* |
|---|---|---|---|
| | *Amperometric end-point* | | |
| 9.210 | bromine | 100.0 | 100.5 |
| | stannous | 99.6 | 100.0 |
| 30.88 | bromine | 100.0 | 99.8 |
| | stannous | 99.5 | 100.0 |
| 43.80 | bromine | 100.0 | 99.8 |
| | stannous | 99.6 | 100.0 |
| 73.79 | bromine | 50.00 | 49.97 |
| | stannous | 49.95 | 49.99 |
| | *Potentiometric end-point* | | |
| 9.982 | bromine | 100.0 | 100.9 |
| | stannous | 99.6 | 100.0 |
| 19.81 | bromine | 100.0 | 99.9 |
| | stannous | 99.8 | 100.0 |
| 31.16 | bromine | 100.0 | 99.6 |
| | stannous | 99.6 | 100.0 |
| 42.77 | bromine | 100.0 | 99.6 |
| | stannous | 99.8 | 100.0 |
| 81.66 | bromine | 50.01 | 49.89 |
| | stannous | 49.87 | 49.96 |

mA/cm$^2$. Amperometric and potentiometric end-point detection both were employed. The equivalence point potential of the bromine–stannous titration is +0.38 V *vs.* S.C.E.

Quinone ($p$-benzoquinone) was chosen as a model organic compound to be titrated with the stannous–bromine system. The curve obtained with a two-electrode amperometric indicating system is shown in Fig. 4 and is typical of the titration of a reversible couple with an irreversible one. The initial current is small, because oxidation of bromide at the indicator anode and reduction of quinone at the indicator cathode take place at potentials farther apart than the impressed voltage (150 mV). As the titration proceeds, the reaction at the indicator anode becomes the oxidation of hydroquinone, and since the quinone–hydroquinone couple is reversible, the indicator current increases. The current reaches a maximum about mid-way through the titration (with indicator electrodes of equal size) and then decreases as more quinone is reduced, the cathode becoming the indicator electrode. Since the stannic–stannous couple is irreversible, the current remains small after the equivalence point.

The fact that the stannous–quinone reaction is somewhat slow renders the direct titration of quinone inconvenient, and a back-titration procedure is preferable. Excess +2 tin was generated, and then the excess was determined by back-titration with bromine.

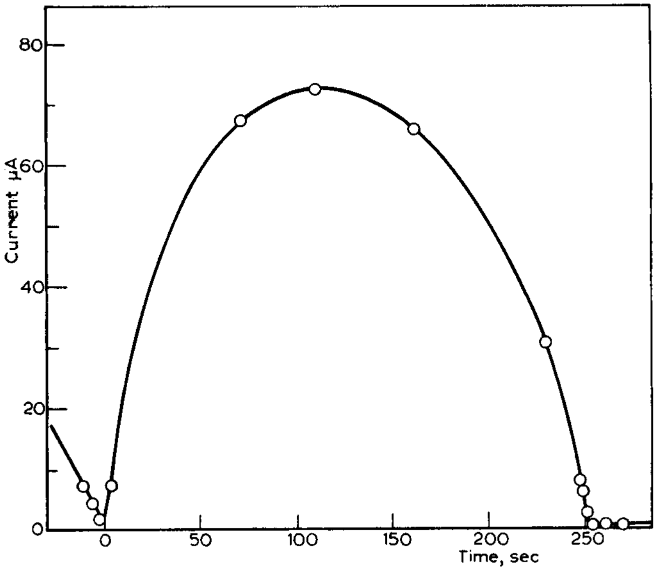

Fig. 4. Amperometric monitoring of coulometric titration of quinone with +2 tin (to the right) and of hydroquinone with bromine (to the left). 3.07 mg of quinone in *ca.* 50 ml of $3M$ sodium bromide, $0.2N$ hydrochloric acid, and $0.2M$ stannic chloride, with 22.8 mA generating current. The two platinum indicator electrodes were subjected to an applied voltage of 150 mV.

TABLE V

COULOMETRIC TITRATION OF QUINONE AND HYDROQUINONE WITH THE STANNOUS–BROMINE SYSTEM

The solution was $3M$ sodium bromide, $0.2M$ stannic chloride, and $0.2N$ hydrochloric acid with a volume of *ca.* 50 ml

| *Sample* | *Current (mA)* | *Quinone (or hydroquinone) taken (mg)* | *Quinone (or hydroquinone) found (mg)* | *% Error* |
|---|---|---|---|---|
| | | *Quinone* | | |
| 1 | 33.24 | 6.138 | 6.108 | —0.5 |
| 2 | 33.20 | | 6.146 | 0.1 |
| 3 | 33.08 | | 6.119 | —0.3 |
| 4 | 33.20 | | 6.124 | —0.2 |
| 5 | 33.16 | | 6.124 | —0.2 |
| | | | mean 6.124 ± 8 | —0.2 |
| | | *Hydroquinone* | | |
| 1 | 33.24 | 6.252 | 6.254 | 0.0 |
| 2 | 33.20 | | 6.270 | 0.4 |
| 4 | 33.20 | | 6.249 | —0.1 |
| 5 | 33.16 | | 6.265 | 0.2 |
| | | | mean 6.259 ± 8 | 0.1 |

The oxidation of hydroquinone by bromine was studied in the same solution by continuation of the back-titration. In this titration the indicator current rises as quinone is produced, and then decreases to a minimum. Past the equivalence point the indicator current again rises because the bromine–bromide couple behaves quasi-reversibly. Bromine was generated slightly past the e.p., and then back-titrated with +2 tin. Bromine does not add to the quinone ring, even at a two-fold excess under these conditions.

In the potentiometric titration of quinone with +2 tin the expected titration curve was obtained, with the equivalence point potential at +0.25 V *vs.* S.C.E. However, the potentiometric titration of hydroquinone with bromine is unsatisfactory, because there is no distinct potential change at the end-point. Because even in the titration of quinone long times were required for the establishment of steady potentials, amperometric end-point detection is preferable in both cases.

Typical results in Table V demonstrate that quinone and hydroquinone can be titrated with the stannous–bromine system with an average error of about ±0.2%.

## ACKNOWLEDGEMENT

Appreciation is expressed to the National Science Foundation for a fellowship held by one of us (A.J.B.).

## SUMMARY

The use of electrolytically generated +2 tin as a coulometric titrant has been studied. In a 3 to $4M$ sodium bromide and $0.2N$ hydrochloric acid solution, containing $0.2M$ stannic chloride, the generation of stannous ion is 100% efficient up to a current density of 80 mA/cm². With this medium iodine and bromine can be titrated coulometrically with errors of about ±0.3% or less. The titration is well suited for the iodometric determination of strong oxidants. Employing stannous ion and bromine for direct and reverse titrations, quinone and hydroquinone have been titrated.

## RÉSUMÉ

On a étudié l'utilisation, pour les titrages coulométriques, de l'étain(II) électrolytiquement formé. On peut ainsi titrer l'iode et le brome et effectuer des dosages iodométriques d'oxydants forts.

## ZUSAMMENFASSUNG

Es wird über coulometrische Titration mit Hilfe von elektrolytisch gebildetem Zinn-(II) berichtet. Beschrieben werden die Titrationen von Brom und Jod sowie die jodometrische Bestimmung starker Oxydationsmittel.

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# A RAPID ROUTINE METHOD FOR THE DETERMINATION OF SUB-MICROGRAM AND MICROGRAM AMOUNTS OF BERYLLIUM IN FILTER PAPER

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## INTRODUCTION

Due to the high toxicity of beryllium, and its increasing use as a nuclear material, the determination of traces of this element is growing in importance. A need exists for a rapid method for the routine determination of submicrogram quantities of beryllium. A method is presented in this paper which allows 20 filter paper smears to be analysed for beryllium in less than 6 hours.

Sodium hydroxide solutions of beryllium fluoresce strongly with 3,5,7,2′,4′-pentahydroxyflavone (Morin)[1]. This reaction provides by far the most sensitive chemical method at present available for the determination of beryllium[2]. Beryllium may be detected at a concentration as low as $5 \cdot 10^{-4}$ p.p.m., and $5 \cdot 10^{-3}$ p.p.m. may be measured with a precision comparable with normal spectrophotometric procedures. The method is, however, subject to many interferences[3], and a preliminary separation of beryllium is usually necessary. The separation has often been accomplished by precipitation of the beryllium as hydroxide or phosphate, using alumunium or iron carrier, followed by a mercury cathode electrolysis[2,4,5]. These procedures are too time-consuming for routine use. Several cation-exchange separations of beryllium have been described[6,7], and a method by NADKARNI, VARDE AND ATHAVALE[8], for the determination of beryllium in ores, was modified in this laboratory for use in the separation of trace amounts of this element. However, these cation-exchange procedures were rejected in favour of a more rapid anion-exchange separation from 9*N* hydrochloric acid. Many metals are retained by a strongly-basic anion-exchange resin from 9*N* HCl[9], whereas beryllium is not, and passes into the effluent. Most foreign elements which also escape the anion-exchange separation do not interfere, or their interference may be removed by complexing with ethylenediaminetetraacetic acid (EDTA).

## APPARATUS

A Hilger "Uvispek" spectrophotometer with fluorimeter attachment was used for all fluorescence measurements. The exciting radiation is provided by a 36 W filament lamp, and the sample cells are of 18 ml capacity. A 365 mμ filter was used to isolate the exciting radiation.

### *Ion-exchange column*

A simple U-tube type ion exchange column[10] was used, of length 11.4 cm and 0.64 cm in diameter while the lead-off capillary tube had an internal diameter of 0.32 cm. A glass-wool plug was used to support the resin, and a 50 ml separatory funnel was attached to the top of the column with a ⧣ B7 joint. The flow-rate was easily controlled by the stop-cock of the separatory funnel. This ion-exchange apparatus is very simple and cheap to construct, and it is convenient in routine work to have a number of such columns arranged in series, so that one column is available per sample.

*Ion-exchange resin*

De-acidite FF. From the Permutit Co., Ltd. London.

*1% sodium stannite solution*

Dissolve 1 g of stannous chloride dihydrate in 100 ml of 1.25$N$ sodium hydroxide by warming gently on a water bath with continuous stirring. This solution must be prepared fresh daily.

*0.025% Morin solution*

B.D.H. grade 3,5,7,2',4' - pentahydroxyflavone was used without further purification. Dissolve 0.25 g in 1 l of 95% ethanol. Store in a refrigerator.

*Quinine sulphate stock solution*

Dissolve 0.125 g of quinine sulphate in 250 ml of water. Add 10 ml of 2$N$ $H_2SO_4$ and dilute to 2 l. Store in a dark bottle.

All other chemicals used were of reagent grade.

## PROCEDURE

Fill the ion-exchange column with water, then add De-acidite FF, as a slurry in water, until the column contains about 2 ml of resin. Place the separatory funnel in position and wash the resin first with 40 ml of water, then with 40 ml of 9$N$ HCl.

Digest the filter paper smear in a small conical flask with 1 ml of $HNO_3$ and 4 ml of $HClO_4$. Evaporate to complete dryness on a hot plate. Dissolve the residue by warming with 10 ml of 9$N$ HCl. Cool, and pass the solution through the ion-exchange column at a rate of 1–2 ml/min. Wash with 40 ml of 9$N$ HCl and evaporate the effluent just to dryness. Dissolve the residue by warming with 5 ml water. Cool, and transfer to a 25-ml volumetric flask. Dilute to the mark with water.

Pipette a suitable aliquot of the sample solution into a small beaker. Dilute to about 25 ml with water. Add 1 ml of 10% EDTA (disodium salt) and neutralise carefully with 10% NaOH, using indicator paper. Transfer the solution to a 50-ml volumetric flask. Add 2 ml of sodium stannite solution, mix, then 1 ml of morin solution.

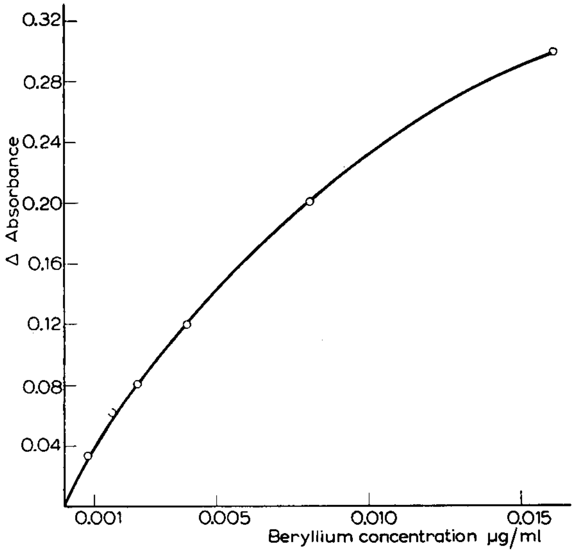

Fig. 1. Determination of beryllium with Morin.

Dilute to volume with water. Prepare a blank in the same manner, substituting water for the sample aliquot. Dilute 2 ml of the quinine sulphate solution to 50 ml in a volumetric flask.

Determine the fluorescence after 15 min and before 60 min by setting the quinine sulphate solution at zero absorbance, then measuring the absorbance of the blank and sample solutions. The $\Delta$ absorbance value (blank absorbance minus sample absorbance) may then be related to beryllium concentration from a calibration curve (Fig. 1). The beryllium content of a blank filter paper, and of the acids used for digestion is usually less than 0.03 $\mu$g.

TABLE I

BERYLLIUM RECOVERY

| *Be taken ($\mu$g)* | *Be found ($\mu$g)* | *% Recovery* |
|---|---|---|
| 0.016 | 0.015 | 94 |
| 0.040 | 0.044 | 110 |
| 0.240 | 0.235 | 98 |
| 0.400 | 0.400 | 100 |
| 0.800 | 0.775 | 97 |
| 4.00 | 3.88 | 97 |

### *Beryllium recovery*

Known amounts of beryllium were subjected to the ion-exchange separation. Table I shows that excellent recoveries may be obtained.

### *Sensitivity of the method*

It may be seen from Fig. 1 that less than 0.05 $\mu$g of beryllium in a paper smear could be detected. LAITINEN AND KIVALO[5] recommend adding sodium sulphate or sodium chloride in a concentration of 1.5 to $2N$ to enhance the beryllium fluorescence. Sodium sulphate was found to be difficult to use at these concentrations, due to its relatively low solubility, and $1.5N$ sodium chloride, at the morin concentration used, actually depressed the fluorescence slightly. In addition, the fluorescence of solutions containing large concentrations of sodium chloride faded much faster than those without added salt. Using the procedure above, the fluorescence showed no appreciable fading for 60 min. A morin concentration of $5 \cdot 10^{-4}$ % in $0.05N$ NaOH was found to be optimum for maximum fluorescence.

### *Effect of diverse ions*

Table II shows the effect of some common cations which were added to a known amount of beryllium and the determination carried out as in the procedure above.

It may be seen that thorium and chromium are the only serious interferences. Copper, zinc, iron and uranium are removed by the ion-exchange column. Calcium and nickel are effectively complexed by EDTA, and aluminium does not interfere in sodium hydroxide solution.

### *Thorium*

Thorium is not retained by De-acidite FF from 9*N* HCl,[9] and does not form a strong complex with EDTA in alkaline solutions. If more than 500 μg of thorium is present in the final solution a precipitate of hydrated thorium oxide forms on the addition of sodium stannite reagent. Low results are then obtained, probably due to co-precipitation of beryllium. Smaller amounts of thorium do not precipitate, and the fluorescence of the solution is then enhanced, leading to high beryllium results. Using the recommended procedure, the maximum permissible concentration of thorium, for an error of less than 5%, is 80 times the beryllium concentration. The use of pyrophosphate, as recommended by SANDELL[3], did not remove the interference of thorium.

### *Chromium*

Chromium interferes seriously, since chromite ion is formed in sodium hydroxide solution, and this appears to strongly absorb U.V. radiation. Chromium(III) was found to be only very weakly adsorbed on De-acidite FF from 9*N* HCl. Chromium (VI) is strongly adsorbed from 1–2*N* HCl, but is quantitatively reduced to the lower valency by 9*N* HCl. The maximum concentration of chromium permissible is 100 times the beryllium concentration.

TABLE II

EFFECT OF DIVERSE IONS

0.400 μg of Be taken in each case

| *Ion added* | *Amount added mg* | *Be found μg* | *Relative error %* |
|---|---|---|---|
| $Ca^{+2}$ | 1.0 | 0.420 | +5 |
| $Ni^{+2}$ | 1.0 | 0.421 | +5 |
| $Al^{+3}$ | 1.0 | 0.385 | —4 |
| $Cu^{+2}$ | 1.0 | 0.377 | —6 |
| $Zn^{+2}$ | 1.0 | 0.388 | —3 |
| $Pb^{+2}$ | 1.0 | 0.400 | 0 |
| $Fe^{+3}$ | 5.0 | 0.393 | —2 |
| $U^{+6}$ | 1.0 | 0.394 | —2 |
| $Th^{+4}$ | 1.0 | 0.248 | —38 |
| $Th^{+4}$ | 0.5 | 0.340 | —15 |
| $Th^{+4}$ | 0.1 | 0.520 | +30 |
| $Th^{+4}$ | 0.02 | 0.402 | 0 |
| $Cr^{+3}$ | 0.5 | 0.041 | —90 |
| $Cr^{+3}$ | 0.25 | 0.128 | —68 |
| $Cr^{+3}$ | 0.05 | 0.387 | —3 |

## ACKNOWLEDGEMENT

It is a pleasure to acknowledge the assistance of Mr. D. B. IZARD with some of the experimental work.

## SUMMARY

A rapid routine method for the determination of submicrogram and microgram amounts of beryllium in filter paper smears is presented. Beryllium is determined fluorimetrically with 3,5,7,2',4' - pentahydroxyflavone (Morin). Many interfering elements are removed by adsorption on a strongly basic anion-exchange resin from 9*N* hydrochloric acid.

*References p. 476*

## RÉSUMÉ

Une méthode fluorimétrique rapide est proposée pour le dosage de traces de béryllium en utilisant la morine comme réactif. De nombreux ions gênants sont éliminés par adsorption sur une résine d'échange d'anions.

## ZUSAMMENFASSUNG

Es wird eine fluorometrische Schnell-methode zur Bestimmung von sehr kleinen Mengen von Beryllium mit Hilfe von Morin als Reagens beschrieben. Eine grosse Anzahl störender Elemente können durch Behandlung mit einem Ionen-Austauscherharz entfernt werden.

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# AMPEROMETRIC TITRATIONS WITH ROTATED PLATINUM ELECTRODE

## I. DETERMINATION OF HYDRAZINE BY POTASSIUM BROMATE

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Amperometric titrations with a rotating platinum electrode have found several useful applications particularly in the determination of halides, cyanides and mercaptans employing silver nitrate and arsenic(III) and other materials employing potassium bromate as reagents[1]. Laitinen and Kolthoff[2] first studied the amperometric titration of trivalent arsenic with potassium bromate in solution $1.0N$ in hydrochloric acid and $0.05M$ in potassium bromide. During the titration the current remains practically zero but increases linearly after the end-point due to the liberation of free bromine by the interaction of excess bromate and bromide:

$$BrO_3^- + 5Br^- \rightarrow 3Br_2 + 3H_2O$$

Hypobromite has also been used for this purpose. The arsenite–bromate reaction was later extended to antimony(III), ammonia and such organic compounds which react rapidly with bromine through substitution or addition. The principal advantages of amperometry at rotating platinum electrode are the feasibility of performing titrations in presence of oxygen and the immediate attainment of steady current values.

Potassium bromate is a powerful oxidizing agent in acidic medium and the titrations are generally performed in the initial presence of bromide. Methyl orange, indigo or other dyestuffs are destroyed by free bromine and serve therefore as irreversible indicators. Reversible indicators, like *p*-ethoxychrysoidine were later discovered and found satisfactory. In general, the indicator errors in bromatometry become appreciable in very dilute solutions and offer therefore a limitation to this titrimetric method of analysis. Under these circumstances, amperometric end-point becomes ideally suitable[3].

Hydrazine is oxidized quantitatively to nitrogen by bromate[4]:

$$3N_2H_4 + 2HBrO_3 \rightarrow 3N_2 + 2HBr + 6H_2O$$

The titration is performed in a 20% hydrochloric acid solution using indigo as indicator[5]. SZEBELLEDY AND MADIS[6] proposed phosphomolybdic acid as indicator in the absence of mineral acids.

In the present work a detailed study has been undertaken to investigate the suitability of and the optimum conditions in employing amperometric end-point in the determination of hydrazine by potassium bromate.

## EXPERIMENTAL

### *Reagents*

Analytically pure hydrazine sulfate and potassium bromate were used to prepare their aqueous solutions. The hydrazine content was ascertained by titration with bromate using *p*-ethoxychrysoidine indicator and also with iodate using chloroform as indicator. Low concentration hydrazine sulfate and bromate solutions were obtained by successive dilution. All the other chemicals used were of the reagent grade.

### *Apparatus*

Sargent's compact unit "Ampot", consisting of dry cell batteries as voltage source, a voltage indicator (0–3 V), and a microammeter (0–20 μA), was used as the amperometric instrument. The microammeter had appropriate shunting resistors for increasing full scale capacity by factors of 1, 2, 4 and 10. A 'safe' position shorts the meter and protects it during preliminary connections and voltage adjustment. A ten-turn potentiometer with dial calibrated in one-thousand units helps in adjusting the applied e.m.f. accurately. The indicator electrode consisted of a piece of platinum wire, 6 to 8 mm in length and 0.5 mm in diameter, sealed into the side of a small bulb blown at the end of a glass tubing. The electrode was rotated at a constant speed of 600 r.p.m. by means of a Bodine motor supplied by Sargent for this purpose. Fischer's saturated calomel electrode served as reference and it was connected to the titrating solution through agar-saturated potassium chloride bridge. Titrations were carried out in a tall beaker of about 150-ml capacity.

### *Procedure*

To an aliquot portion of hydrazine sulfate transferred into the titration beaker, a sufficient quantity of hydrochloric acid to maintain its overall normality $2N$ and 10 ml $0.5M$ potassium bromide solution were added, and the total volume brought to 100 ml with water. The rotating platinum electrode was made the cathode and the saturated calomel the anode. The current multiplier switch was kept in the lowest multiplier position and no external e.m.f. was applied across the electrodes. The initial current, which was generally slightly more than zero, was noted and the titration commenced with $0.1N$ $KBrO_3$. After the end-point 6–8 increments of 0.05 or 0.1 ml of the reagent were added and the current measured. For smaller quantities of hydrazine, 0.01 or 0.001$N$ bromate was used and the current measured at multiplier position of 2 or 1. A plot of the reagent volume added *versus* the current in microamperes results in a reversed L-type of graph and gives the experimental end-point.

A typical titration curve is shown in Fig. 1 and a representative set of data for the estimation of hydrazine is entered in Table I. It will be seen that the experimental results are in close agreement with those anticipated on the basis of standard method using iodate or bromate.

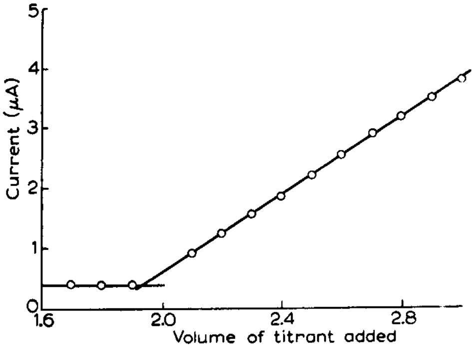

Fig. 1. Amperometric titration of 5 ml $0.9940 \cdot 10^{-3} M$ hydrazine sulfate with $0.01027 N$ $KBrO_3$. End-point: theoretical 1.9325 ml; from graph 1.935 ml.

TABLE I

DETERMINATION OF HYDRAZINE BY POTASSIUM BROMATE

| *Hydrazine sulfate molarity, M* | *Hydrazine, mg* | | *Difference mg* |
|---|---|---|---|
| | *Calculated* | *Found* | |
| $0.9915 \cdot 10^{-1}$ | 3.177 | 3.152 | 0.027 |
| $0.9940 \cdot 10^{-2}$ | 1.593 | 1.588 | 0.005 |
| $0.9940 \cdot 10^{-2}$ | 0.6372 | 0.6420 | 0.0048 |
| $0.9940 \cdot 10^{-2}$ | 0.3186 | 0.3210 | 0.0024 |
| $0.9940 \cdot 10^{-3}$ | 0.09558 | 0.09547 | 0.0011 |
| $0.9940 \cdot 10^{-3}$ | 0.06372 | 0.06336 | 0.0036 |
| $0.9940 \cdot 10^{-3}$ | 0.03186 | 0.03210 | 0.00024 |
| $0.9940 \cdot 10^{-4}$ | 0.01593 | 0.01678 | 0.00085 |
| $0.9940 \cdot 10^{-4}$ | 0.003186 | 0.003360 | 0.000174 |

## DISCUSSION

A series of experiments carried out to study the influence of acidity on the oxidation of hydrazine by bromate revealed that the titration could be performed accurately in an overall concentration of hydrochloric acid maintained between 0.5 and 4$N$ (see Table II). In the ordinary titrations with indicator, a minimum hydrochloric acid content of 2$N$ is recommended while in the SZEBELLEDY-MADIS procedure interference is caused by the presence of mineral acids. At lower concentrations of hydrochloric acid than 2$N$, hydrazine tends to undergo side reactions such as the formation of hydrazoic acid and ammonia[3]. Quantitative results at an acidity as low as 0.5$N$ hydrochloric acid in the present work may be attributed to the inherent difference in

*References p. 480*

TABLE II

EFFECT OF HYDROCHLORIC ACID CONCENTRATION

| *Overall normality of HCl, N* | *Hydrazine, mg* | |
|---|---|---|
| | *Calculated* | *Found* |
| 0.5 | 0.1593 | 0.1588 |
| 0.5 | 1.593 | 1.588 |
| 1.0 | 0.1593 | 0.1588 |
| 1.5 | 0.1593 | 0.1588 |
| 2.0 | 0.1593 | 0.1588 |
| 3.0 | 0.1593 | 0.1588 |
| 4.0 | 0.1593 | 0.1588 |
| 4.0 | 1.593 | 1.588 |

amperometry and the titration using indicators. In the latter, titration before and near the end-point is performed slowly — a circumstance in which hydrazine is susceptible towards side reactions. In amperometric titration, however, a slight excess of bromate is added which converts hydrazine rapidly to nitrogen and the current readings corresponding to the increments of bromate only after the end-point are of significance. No systematic study seems to have been made using sulfuric in place of hydrochloric acid in the oxidation of hydrazine by bromate. Accurate results were obtained when the total sulfuric acid concentration was adjusted between 1 and 5*N* (see Table III). This reaction appears to be slightly slower than in hydrochloric acid.

The initial presence of bromide in the system helps in eliminating the first stage of bromate reaction, $BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$, so that only the second reaction, $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$, is involved. In conformity with earlier observations by LAITINEN AND KOLTHOFF[2] on the arsenite–bromate reaction, an optimum overall concentration of 0.05*M* potassium bromide is preferable. Larger quantities of bromide have, however, little adverse effect.

TABLE III

EFFECT OF SULFURIC ACID CONCENTRATION

| *Overall normality of $H_2SO_4$, N* | *Hydrazine, mg* | |
|---|---|---|
| | *Calculated* | *Found* |
| 1.0 | 0.1593 | 0.1588 |
| 1.0 | 1.593 | 1.588 |
| 2.0 | 0.1593 | 0.1588 |
| 3.0 | 0.1593 | 0.1588 |
| 4.0 | 0.1593 | 0.1588 |
| 5.0 | 0.1593 | 0.1588 |
| 5.0 | 1.593 | 1.588 |

The amperometric titration of hydrazine with bromate can be effected at an applied potential between 0 and 0.3 *V versus* the S.C.E. It is, however, simple to perform the titration at an applied external e.m.f. of zero.

The optimum conditions for the amperometric determination of hydrazine by bromate are: 2*N* hydrochloric acid, 0.05*M* potassium bromide and an applied e.m.f.

of zero *versus* S.C.E. By adjusting the bromate concentration about ten times of hydrazine the volume changes will be negligible. For very precise work and when handling smaller volumes, it is advisable to apply volume correction as follows[7]:

$$i_{\text{corr.}} = i_{\text{meas.}} \left(\frac{V + v}{V}\right)$$

where $V$ denotes the original volume of the solution titrated and $v$ the reagent volume added at any point. Under the given experimental conditions, it was possible to titrate $1 \cdot 10^{-1}$ to $1 \cdot 10^{-3} M$ hydrazine sulfate solution corresponding to about 0.03–3 mg of hydrazine within a very reasonable accuracy. At higher dilutions of the order of $1 \cdot 10^{-4} M$ and containing about 3 μg hydrazine, the titration could still be performed but with an error of nearly 5%. At such low concentrations of hydrazine, titrations either with indicator or by other electrometric methods do not yield trustworthy results. It may be pointed out that the present amperometric method particularly for the micro-estimation of hydrazine by standard $KBrO_3$ is accurate, rapid, and simple besides being independent of visual color changes.

Further work on the bromatometric determination of phenylhydrazine, semicarbazide and other oxidizable materials on similar lines is in progress.

## ACKNOWLEDGEMENT

We are indebted to Boyd Professor Dr. PHILIP W. WEST for research facilities and interest in the work.

## SUMMARY

The reaction between hydrazine and potassium bromate is studied amperometrically at rotating platinum electrode. The bromate titration is performed at an applied e.m.f. of zero (*versus* S.C.E.) and in the presence of bromide and 1–5$N$ sulfuric acid or 0.5–4$N$ hydrochloric acid. Quantities ranging from 30 μg to 3 mg of hydrazine can be estimated accurately by this method. Determination of phenylhydrazine, semicarbazide and other oxidizable materials on similar lines is suggested.

## RÉSUMÉ

On a étudié la réaction entre l'hydrazine et le bromate de potassium, par ampérométrie, au moyen d'une électrode de platine tournante. L'hydrazine peut ainsi être dosée avec précision. Un dosage est proposé pour la phénylhydrazine, la semicarbazide et d'autres substances analogues.

## ZUSAMMENFASSUNG

Die Reaktion zwischen Hydrazin und Kaliumbromat wurde amperometrisch mit Hilfe einer rotierenden Platinelektrode untersucht. Nach dieser Methode lässt sich Hydrazin sehr genau bestimmen. Ihre Anwendungsmöglichkeit bei Phenylhydrazin, Semicarbazid und anderen ähnlichen Verbindungen wird geprüft werden.

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# THE AMPEROMETRIC AND CONSTANT CURRENT POTENTIOMETRIC TITRATION OF ETHYLENEDIAMINETETRAACETIC ACID WITH COPPER (II)

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PRIBIL AND MATYSKA[1], ACKERMANN AND SCHWARZENBACH[2], AND REILLY, SCRIBNER, AND TEMPLE[3] reported the amperometric titration of ethylenediaminetraacetic acid (EDTA) with copper(II) at the dropping mercury electrode. TANAKA, KODAMA, SASKI, AND SUGINO[4] titrated copper with EDTA in an acetate buffer of pH 4.2 using the dropping mercury electrode.

NIKELLEY AND COOKE[5] used the mercury-pool indicator electrode for the EDTA titration of micromolar solutions of copper. In favorable cases, titrations were successfully carried out at concentrations approaching $10^{-7}M$.

PRIBIL, KOUDELA, AND MATYSKA[6] used a platinum–calomel electrode pair to titrate copper(II) by adding a known quantity of EDTA and back-titrating the excess with iron(III). BELCHER, GIBBONS, AND WEST[7] have shown that copper could be titrated directly with EDTA using this electrode system. POLYAK[8] has applied this electrode system to the determination of copper in electrolyte baths.

SIGGIA, EICHLIN, AND RHEINHART[9] used the platinum–calomel and the mercury coated platinum–calomel electrode pairs to titrate $0.1M$ copper with EDTA.

REILLEY[10] proposed the use of a mercury electrode for the potentiometric end-point detection in EDTA titrations. SADEK AND REILLEY[11] adapted the mercury electrode method to ultramicro chelometric titrations. The mercury electrode was also employed by POLCIN[12] for the EDTA titration of copper. SAJO[13] used zinc as the back-titrant for the potentiometric determination of copper.

Bimetallic electrode systems also have been employed. BUDANOVA AND PLATONOVA[14] have reported the determination of copper by adding excess EDTA and back-titrating with lead ions using the platinum–tungstan system.

Copper(II) was titrated automatically by HASLAM, SQUIRRELL, AND HESKINS[15] using disodium dihydrogen ethylenediaminetetraacetate. The end-point was taken as the point where the pH did not change upon further addition of the titrant.

NIGHTINGALE[16] reported the potentiometric titration as small constant current of EDTA with copper using the platinum electrode.

KOLTHOFF[17] proposed the amperometric titration of ethylenediaminetetraacetic acid with copper(II) at the rotated platinum electrode. The rotated platinum electrode is more desirable then a dropping mercury electrode as an indicator electrode because of its convenience in handling and greater sensitivity.

The amperometric titration proposed by KOLTHOFF and the constant current potentiometric titration of NIGHTINGALE, both using the rotated platinum electrode as indicator electrode, were tried in an acidic solution, rather than in basic solutions used by the majority of the above researchers.

## MATERIALS

Standard copper(II) solutions were prepared by solution of No. 18 electrolytic copper wire obtained from the Melins Co., Cleveland, Ohio, in a minimum amount of nitric acid, followed by dilution to volume.

Standard solutions of EDTA were prepared by dissolving "Baker Analyzed" disodium dihydrogen ethylenediaminetetraacetate dihydrate obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J., in water and standardizing against standard copper using Murexide as an indicator.

All chemicals were reagent grade.

## APPARATUS

The Sargent Manual Polarograph, Model III, made by E. H. Sargent and Co., Chicago, Ill., and a manual polarograph constructed in the Rensselaer Polytechnic Institute Chemistry Department were used. The rotated platinum wire micro electrode was made of No. 18 platinum wire with 0.5 cm exposed to solution. It was driven at 600 r.p.m. by a Sargent Synchronous Motor, Type KYC-22.

Potentials were measured with a Triplett Model 620 VTVM, Serial No. 6691. The current for the constant current potentiometric titrations was supplied through a large series resistor by a $1\frac{1}{2}$-V battery.

## PROCEDURE

Polarograms of the copper–EDTA titration were run in a $0.2M$ acetate buffer of pH 5.0 at different points in the titration using the rotated platinum micro electrode (R.P.E.) *versus* the saturated calomel electrode (S.C.E.) with the manual polarograph built at Rensselaer Polytechnic Institute. Typical polarograms are shown in Fig. 1, where A is 50% to end-point, B is 1% before end-point, and C is 1% after end-point in the titration of EDTA with Cu(II). The solutions were degassed with a glass-frit bubbler for 15 min with nitrogen before each polarogram and continously during the polarogram. For all experiments, the platinum electrode was cleaned by washing with conc. nitric acid and then placed in distilled water and shorted to the S.C.E. until no current flowed through the circuit formed.

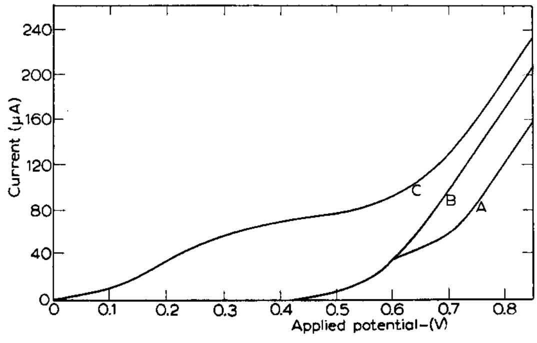

Fig. 1. Polarograms of Cu–EDTA titration.

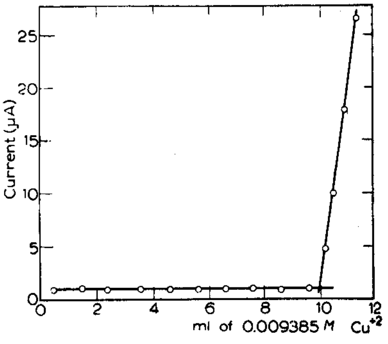

Fig. 2. Amperometric titration of EDTA.

The amperometric titration of EDTA with copper(II) was performed in a 100-ml beaker containing 50 ml of buffer and 10 ml of EDTA solution using the R.P.E. at an applied potential of about —0.45 V *vs.* S.C.E.

*References p. 485*

The solutions were degassed with a glass-frit bubbler for 15 min with nitrogen before each titration and continously during the titration. The titrant was added in 1-ml increments before the end-point region and 0.2-ml increments in and after the end-point region. In all titrations, except the last three sets of data where two minute intervals were used, one minute intervals were taken between addition of reagent and reading of current. The constant potential was supplied by and the current was read with the manual polarograph built at Rensselaer Polytechnic Institute except for the last three sets of data where the Sargent Manual Polarograph was used.

A typical amperometric titration graph is shown in Fig. 2 .The end-point was taken as the intersection of the two straight lines.

The potentiometric titration at small constant current of EDTA with copper(II) was performed in a 100 ml beaker containing 50 ml buffer and 10 ml of EDTA solution using the R.P.E. *vs.* S.C.E. The solution was degassed with nitrogen dispersed through a glass-frit bubbler for 15 min before each experiment and continously during the titration. The titrant was added in 2-ml increments before the end-point region and in 2-drops increments in the end-point region. In all titrations, one minute intervals were taken between addition of reagent and reading of potential. The constant current was supplied by $1\frac{1}{2}$-V battery, and the potential was read with the Triplett VTVM.

A typical constant current potentiometric titration graph is shown in Fig. 3. The end-point was determined either from the inflection point on a graphical plot or by interpolation between readings at the point of steepest potential break.

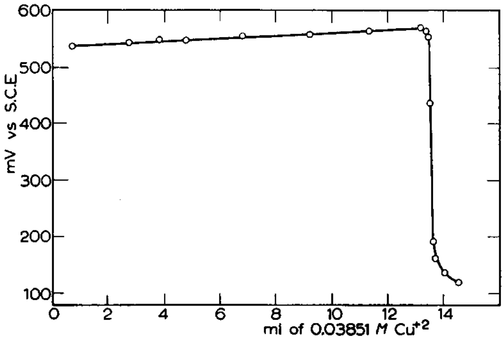

Fig. 3. Potentiometric titration of EDTA.

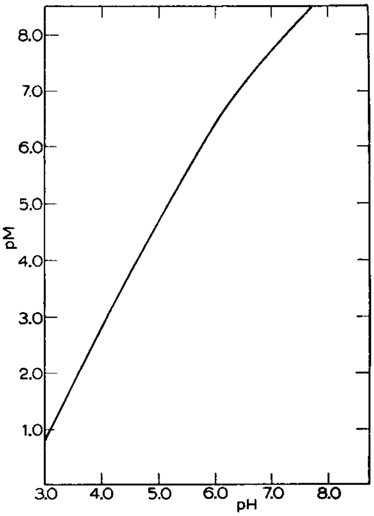

Fig. 4. pM *vs.* pH.

## RESULTS

The experimental results are given in Tables I and II.

*References p. 485*

TABLE I

AMPEROMETRIC TITRATION

| *App. pot. (—E) (V)* | *Taken (μequiv.)* | *No. of det.* | *Found (μequiv.)* | *S.D. (%)* | *Buffer* | *pH* |
|---|---|---|---|---|---|---|
| 0.50 | 983.6 | 5 | 981.2 | 0.20 | 0.1*M* acetate<br>0.1*M* KNO$_3$ | 5.0 |
| | 983.6 | 2 | 980.1 | 0.20 | | 5.0 |
| 0.45 | 717.0 | 8 | 718.5 | 0.64 | 0.2*M* acetate | 5.0 |
| | 983.6 | 6 | 983.2 | 0.30 | | 5.0 |
| | 358.5 | 6 | 358.7 | 0.50 | | 5.0 |
| | 179.2 | 6 | 179.0 | 0.67 | | 5.0 |
| | 98.4 | 2 | 97.8 | 0.70 | | 4.73 |
| | 98.4 | 2 | 98.1 | 0.70 | | 5.73 |
| | 49.2 | 4 | 49.2 | 0.41 | | 5.0 |
| | 9.84 | 4 | 9.84 | 0.41 | | 5.0 |
| | 0.984 | 2 | 0.801 | N.D. | | 5.0 |

TABLE II

CONSTANT CURRENT POTENTIOMETRIC TITRATION

| *App. current (μA)* | *Taken (μequiv.)* | *No. of det.* | *Found (μequiv.)* | *S.D. (%)* | *Buffer* | *pH* |
|---|---|---|---|---|---|---|
| 5 | 983.6 | 5 | 984.3 | 0.12 | 0.2*M* acetate | 5.0 |
| 2 | 245.9 | 6 | 246.0 | 0.40 | | 5.0 |
| | 98.4 | 6 | 98.2 | 0.20 | | 5.0 |
| 1 | 49.2 | 6 | 48.9 | 0.20 | | 5.0 |

## DISCUSSION

The experimental results for the amperometric titration show that this titration can be used to titrate from 983.6 down to 9.84 μequiv. of EDTA in about 70 ml of solution with copper(II) at the R.P.E. in an acetate buffer of pH 5.0 These amounts correspond to a concentration range of $7 \cdot 10^{-3}$ to $7 \cdot 10^{-5} M$ EDTA. The results also show that when 98.4 μequiv. were taken ($7 \cdot 10^{-4} M$ EDTA), a pH of 4.73 and 5.73 did not change the amount of EDTA found to a significant degree.

When 0.984 μequiv. ($7 \cdot 10^{-6} M$) of EDTA were titrated in an acetate buffer of pH 5.0, the amount found did not compare well with the amount taken because the EDTA at this low concentration and at this pH does not completely complex the copper.

The stability constant, *K*, for the fundamental reaction

$$Cu^{+2} + Y^{-4} \rightleftharpoons CuY^{-2}$$

where Cu$^{+2}$ is the copper(II) ion and Y$^{-4}$, the fully ionized ethylenediaminetetraacetate ion, is

$$K = (CuY^{-2}) \;/\; (Cu^{+2})\,(Y^{-4}).$$

The stability constant for the copper–EDTA complex is $10^{18.8}$. The apparent stability constant at a particular pH may be calculated by dividing *K* by *α*, the fraction of EDTA which is present as Y$^{-4}$ (and not as other dissociated states of H$_4$Y).

$\alpha = 1 + (H^+) / K_4 + (H^+)^2 / K_4K_3 + (H^+)^3 / K_4K_3K_2 + (H^+)^4 / K_4K_3K_2K_1$ where $K_4$, $K_3$, $K_2$, and $K_1$ are the acidity constants of EDTA.

*References p. 485*

Since a concentration less than about $7 \cdot 10^{-5} M$ EDTA could not be titrated at a pH of 5.0, the above equations were used to calculate a complexed copper to uncomplexed copper ratio, at the end-point, below which the titration would not go to completion. This ratio was found to be $10^4$. Using this ratio, the minimum concentration of EDTA that could be titrated with copper(II) (or *vice versa*) at a given pH was determined for several pH values. These values are plotted in Fig. 4 as log of minimum concentration, pM, *versus* pH.

The experimental results for the potentiometric titration at small constant current of EDTA with copper(II) at the R.P.E. show that this titration can be used to determine 983.6 to 49.2 μequiv. of EDTA in about 70 ml of solution ($7 \cdot 10^{-3}$ to $3.5 \cdot 10^{-4} M$ EDTA). In all experiments, a very sharp potential break of about 0.3 V occurred at the end-point.

An applied current of 5 μA may be a little high for titrating below about 500 μequiv. in 70 ml of solution since the amount of free copper(II) required to give a diffusion current of this size is a little beyond the end-point and will be further beyond the end-point as the concentration of EDTA in solution is decreased in subsequent titrations. An applied current of 1-2 μA is recommended.

## SUMMARY

The amperometric titration of $7 \cdot 10^{-5} M$ EDTA with copper(II) was performed in an acetate buffer of pH 5.0 at the rotated platinum electrode. A pH range of 4.73 to 5.73 was used to titrate $7 \cdot 10^{-4} M$ EDTA. The potentiometric titration at small constant current of $7 \cdot 10^{-3}$ to $3.5 \cdot 10^{-4} M$ EDTA with copper(II) was performed in an acetate buffer of pH 5.0 at the rotated platinum electrode.

## RÉSUMÉ

Un titrage ampérométrique et un titrage potentiométrique de l'acide éthylènediaminotétraacétique, par le cuivre(II), ont été effectués en milieu tampon à l'électrode tournante de platine.

## ZUSAMMENFASSUNG

Es wird eine amperometrische und potentiometrische Titration von Äthylendiaminotetraessigsäure mit Cu-(II) in gepufferter Lösung an einer rotierenden Platinelektrode beschrieben.

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# EFFECT OF GELATIN AND POLYOXYETHYLENE LAURYL ETHER ON POLAROGRAPHIC DIFFUSION CURRENTS OF SOME INORGANIC IONS*

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In polarography, some surface-active substances are generally used to suppress the maximum in the current–voltage curve. Gelatin has been known as one of the best maximum suppressors. Although gelatin is very effective and widely used for this purpose, it has a disadvantage that the addition of gelatin of relatively high concentration decreases the diffusion current of many electroactive species. Furthermore, gelatin is rapidly deteriorated and its stock solution must be renewed quite frequently. In order to overcome these deficiencies of gelatin, the use of certain kinds of synthetic detergents as a maximum suppressor has been widely examined[1], and polyoxyethylene lauryl ether (LEO), which is a non-ionic detergent, has been expected to be very useful in the polarographic analysis[2].

The effect of gelatin on the diffusion current was already reported by some investigators and was explained by assuming the combination between electroactive species and gelatin molecules[3,4]. This evidence was also applied to the study of the interaction of electroactive species with gelatin molecules[5,6]. However, no systematic study on the effect of gelatin on diffusion currents at the conventional dropping mercury electrode (DME) has been found in the literature. In this paper, the effect of gelatin and LEO on the diffusion currents of several inorganic reducible ions is presented, and the potentiality of LEO as a maximum suppressor is discussed.

## APPARATUS AND REAGENTS

Current-voltage curves were measured either by a Shimadzu RP-II pen-recording polarograph or by a manual polarograph[7], the latter of which was used for the accurate determination of the diffusion current. A mercury pool electrode of a large area in a saturated potassium chloride solution connected to the cell solution by a HUME AND HARRIS-type salt bridge[8] was employed as the anode, and a saturated calomel electrode was used as a reference electrode to measure the electrode potential of the DME. The drop time and the rate of flow of mercury of the DME were measured under the same conditions as those in the determination of diffusion current constants.

The differential capacity of the DME was measured by an impedance bridge similar to that of GRAHAME[9]. The balance of the bridge was determined just before the detachment of the mercury drop from the tip of the capillary. In this case, the DME of relatively long drop time was used. Its drop time and rate of flow of mercury were 8.62 sec and 0.906 mg/sec, respectively, in an air-free 0.1*M* potassium nitrate solution at —0.5 V *vs.* S.C.E.

The relative viscosity of the solution was measured by using a U-type Ostwald viscosimeter, through which 10.0 ml of distilled water flowed in 39.5 sec at 25°.

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All measurements were carried out in a thermostat of 25.0 ± 0.1°.

The standard solutions of cadmium and zinc were prepared by dissolving known amounts of pure cadmium and zinc metals in distilled nitric acid and hydrochloric acid, respectively. The sample of LEO of high purity was kindly prepared by Nedzu Chemical Laboratory, Tokyo; it has a chemical formula of $C_{12}H_{25}O(C_2H_4O)_nOH$, where $n$ is about 15*. All other chemicals were of analytical reagent grade, and redistilled water was used to prepare the solutions of the desired concentration. The stock solution of ferric ammonium sulfate was kept in a brown bottle, and the polarographic measurement of trioxalatoferrate(III) ions was carried out in a cell made of brown glass.

## RESULTS AND DISCUSSION

### *Adsorbability and maximum suppression point of LEO*

It is necessary that a maximum suppressor be adsorbed on the surface of the DME over a wide range of the electrode potential. The previous paper[2] showed from the experimental results on the electrocapillary curve that LEO is very surface-active in 0.1$M$ potassium chloride solution. The adsorption of LEO on the DME in 0.1$M$ potassium nitrate solution was also studied by measuring the differential capacity of the electrode at various electrode potentials, some results of which are shown in Fig. 1. In general, the capacity, measured at the ordinary DME, of such a substance of relatively large molecular weight as LEO can not be considered as that corresponding to the equilibrium state of the adsorption.[10] However, it can be concluded from the results in Fig. 1 that LEO strongly adsorbs on the surface of the DME over the potential range from 0 to —1.6 V *vs.* S.C.E. in 0.1$M$ potassium nitrate solution.

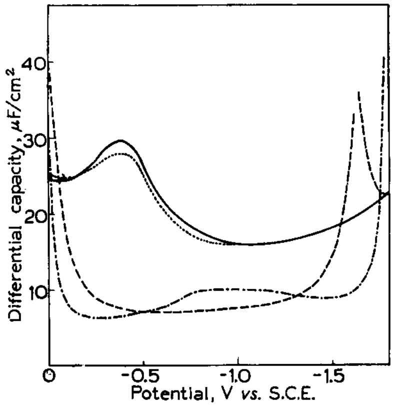

Fig. 1. Differential capacity of LEO solutions containing 0.1$M$ KNO$_3$ at 25°: —, 0.1$M$ KNO$_3$; . . ., $2 \cdot 10^{-6}M$ LEO; — —, $5 \cdot 10^{-4}M$ LEO; —.—, $1 \cdot 10^{-3}M$ LEO.

The ability of surface-active substances to suppress the maximum can be conveniently examined by measuring their maximum suppression points (MSP)[11] for various electroactive species. The MSP is defined as the minimum concentration of

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[*] A similar sample can be obtained from Nikko Co., Tokyo, under the trade name of "Nikkol BL-10".

the surface-active substance which is necessary to make the maximum current, $i_m$, equal to the limiting (diffusion) current, $i_l$; it was determined graphically by plotting $i_m/i_l$ against the logarithm of the concentration of the surface-active substance. The MSP's of LEO for some reducible ions are shown in Table I. It was found that the MSP's of LEO generally increase with the increase of the concentration of reducible ions or with the decrease of the concentration of indifferent electrolytes (Tables II and III).

TABLE I

MSP'S OF LEO FOR SOME REDUCIBLE IONS

| *Reducible ions* | *MSP, M* |
|---|---|
| 1 m$M$ Cu(II) in 0.1$M$ $KNO_3$ | $4.1 \cdot 10^{-5}$ |
| 3 m$M$ Pb(II) in 0.1$M$ KCl[a] | $1.3 \cdot 10^{-6}$ |
| 3 m$M$ Ni(II) in 0.1$M$ KCl[a] | $1.0 \cdot 10^{-6}$ |
| 1 m$M$ Co(II) in 0.1$M$ KCl | $1.2 \cdot 10^{-6}$ |

[a] Data from ref. [2].

TABLE II

MSP'S OF LEO FOR VARIOUS CONCENTRATIONS OF COPPER(II) AND COBALT(II) IONS

| *Cu(II)*[a] | | *Co(II)*[b] | |
|---|---|---|---|
| *Concn. of Cu(II) ion mM* | *MSP M* | *Concn. of Co(II) ion mM* | *MSP M* |
| 0.6 | $2.7 \cdot 10^{-6}$ | 0.4 | $2.5 \cdot 10^{-7}$ |
| 0.8 | $5.2 \cdot 10^{-6}$ | 0.5 | $6.5 \cdot 10^{-7}$ |
| 0.9 | $1.1 \cdot 10^{-5}$ | 1.0 | $1.2 \cdot 10^{-6}$ |
| 1.0 | $4.1 \cdot 10^{-5}$ | 1.2 | $1.4 \cdot 10^{-6}$ |
| 2.0 | $1.1 \cdot 10^{-4}$ | 2.5 | $3.2 \cdot 10^{-6}$ |
| 3.0 | $1.6 \cdot 10^{-4}$ | 3.8 | $4.1 \cdot 10^{-6}$ |
| 5.0 | $2.0 \cdot 10^{-4}$ | 7.5 | $7.0 \cdot 10^{-6}$ |

[a] In 0.1$M$ potassium nitrate solution.
[b] In 0.1$M$ potassium chloride solution.

TABLE III

MSP'S OF LEO FOR 0.3 m$M$ OF COPPER(II) AND COBALT(II) IONS IN VARIOUS CONCENTRATIONS OF INDIFFERENT SALTS

| *Concn. of indifferent salts M* | *MSP, M* | |
|---|---|---|
| | *Cu(II)*[a] | *Co(II)*[b] |
| 0.03 | $3.2 \cdot 10^{-6}$ | $2.4 \cdot 10^{-6}$ |
| 0.05 | $1.4 \cdot 10^{-6}$ | $1.1 \cdot 10^{-6}$ |
| 0.1 | $8.5 \cdot 10^{-8}$ | $1.7 \cdot 10^{-7}$ |
| 0.2 | 0 | $3.1 \cdot 10^{-8}$ |
| 0.3 | 0 | 0 |

[a] In potassium nitrate solution.
[b] In potassium chloride solution.

It can be concluded from these experimental results that many polarographic maxima of the first kind are effectively suppressed by the addition of LEO less than $1 \cdot 10^{-5} M$. In the case of copper-maximum in $0.1 M$ potassium nitrate solution, however, the MSP of LEO is relatively high, i.e., of the order of $10^{-5}$ to $10^{-4} M$. This may be attributed to the fact that the potential, where the maximum of copper ion appears, is almost identical with the desorption potential of LEO in the positive branch of the electrocapillary curve (Fig. 1).

### *Effect of gelatin and LEO on current–voltage curves*

The presence of surface-active substances generally increases the overpotential of the electrode reaction and distorts the shape of the current–voltage curve. Some experimental results on the effect of surface-active substances on the polarographic current–voltage curve were reported in the previous paper[2]. In the case of copper(II) ions in $0.1 M$ potassium nitrate solution, a minimum of the current appeared in the potential region of the electrocapillary maximum, when the concentration of LEO or gelatin was higher than 0.05 m$M$ or 0.02%, respectively (Fig. 2). Similar phenomena were also observed in the polarographic reduction of trioxalatoferrate(III) ions in $0.5 M$ potassium oxalate solution, which contradicts HEYROVSKY's theory on the electrode reaction to the effect that the electrode reaction involving only one electron in the electron-transfer process is not affected by the presence of surface-active substances[12]. The effect of LEO on the electrode reaction was found to be larger than that of gelatin in all cases. These results can be reasonably explained by assuming the retardation of the electrode reaction due to the presence of the adsorbed film of surface-active substances on the surface of the DME[13]. The details will be discussed elsewhere.

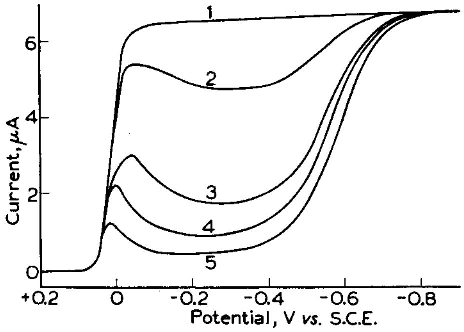

Fig. 2. Effect of LEO on the polarographic reduction wave of 1 m$M$ Cu(II) ion in $0.1 M$ $KNO_3$ solution: 1, $2 \cdot 10^{-5} M$; 2, $5 \cdot 10^{-5} M$; 3, $1 \cdot 10^{-4} M$; 4, $2 \cdot 10^{-4} M$; 5, $1 \cdot 10^{-3} M$ LEO.

### *Effect of gelatin and LEO on diffusion currents*

Diffusion current constants, $I$, of some metal ions were determined in the solution containing various concentrations of gelatin or LEO by using the relation[14]:

$$I = \frac{i_d}{C\, m^{2/3}\, t^{1/6}}$$

where $i_d$ is the diffusion current in μA, $C$ the bulk concentration of the reducible ion in m$M$ and $m$ and $t$ are the rate of flow of mercury in mg/sec and the drop time in sec, respectively, at the electrode potential where $i_d$ is measured. An example of the experimental data is presented in Table IV. Tables V and VI clearly indicate that the presence of gelatin generally decreases the value of diffusion current constants when its concentration is higher than 0.05%, while the presence of LEO does not change the value of diffusion current constants over the wide concentration range of LEO.

The effect of viscosity of the solution must be considered as one of the reasons for the change of diffusion current constants[15]. The relative viscosity of 0.1 $M$ potassium nitrate solution containing 1 m$M$ LEO was found to be only 0.4% larger than that of 0.1$M$ potassium nitrate solution. On the other hand, the addition of 0.4% gelatin increased the relative viscosity of 0.1$M$ potassium nitrate solution about 19% as shown in Table VII. However, it has been known that the change of viscosity of the solution due to the presence of lyophilic colloids such as gelatin does not affect the

TABLE IV

DIFFUSION CURRENTS, DIFFUSION CURRENT CONSTANTS AND CHARACTERISTICS OF THE DME IN THE SOLUTION CONTAINING 1.00 m$M$ CADMIUM ION, 0.1$M$ POTASSIUM NITRATE AND VARIOUS CONCENTRATIONS OF GELATIN

| *Concn. of gelatin* % | *Drop time (t) sec* | *Rate of flow of mercury (m) mg/sec* | $m^{2/3}t^{1/6}$ | *Diffusion current* ($i_d$) $\mu A$ | *Diffusion current const. (I)* |
|---|---|---|---|---|---|
| 0.001 | 4.80 | 1.76 | 1.89 | 6.28 | 3.32 |
| 0.002 | 4.73 | 1.74 | 1.86 | 6.22 | 3.34 |
| 0.005 | 4.73 | 1.76 | 1.87 | 6.28 | 3.36 |
| 0.01 | 4.50 | 1.76 | 1.86 | 6.18 | 3.33 |
| 0.02 | 4.35 | 1.77 | 1.87 | 6.18 | 3.31 |
| 0.05 | 4.35 | 1.76 | 1.86 | 5.97 | 3.21 |
| 0.1 | 4.34 | 1.74 | 1.84 | 5.88 | 3.20 |
| 0.2 | 4.33 | 1.77 | 1.87 | 5.71 | 3.05 |
| 0.4 | 4.33 | 1.74 | 1.84 | 5.31 | 2.88 |

TABLE V

DIFFUSION CURRENT CONSTANTS OF REDUCIBLE IONS IN THE SOLUTION CONTAINING VARIOUS CONCENTRATIONS OF GELATIN

| *Concn. of gelatin* % | *Diffusion current constant* | | | | | |
|---|---|---|---|---|---|---|
| | *Tl(I)*[a] | *Pb(II)*[a] | *Pb acetate*[b] | *Cd(II)*[a] | *Zn(II)*[a] | *Co(II)*[a] |
| 0.001 | 2.67 | 3.56 | 2.88 | 3.32 | 3.33 | 3.46 |
| 0.002 | 2.67 | 3.60 | — | 3.34 | 3.35 | 3.49 |
| 0.005 | 2.69 | 3.63 | — | 3.36 | 3.37 | 3.46 |
| 0.01 | 2.68 | 3.43 | 2.83 | 3.33 | 3.38 | 3.50 |
| 0.02 | 2.70 | 3.50 | — | 3.31 | 3.37 | 3.40 |
| 0.05 | 2.66 | 3.45 | — | 3.21 | 3.31 | 3.34 |
| 0.1 | 2.66 | 3.14 | 2.85 | 3.20 | 3.28 | 3.27 |
| 0.2 | 2.66 | 2.92 | 2.85 | 3.05 | 3.14 | 3.13 |
| 0.4 | 2.63 | — | 2.82 | 2.88 | 3.00 | 3.01 |

[a] In 0.1$M$ potassium nitrate solution.
[b] In acetate buffer solution of pH 4.9.

TABLE VI

DIFFUSION CURRENT CONSTANTS OF REDUCIBLE IONS IN 0.1*M* POTASSIUM NITRATE SOLUTIONS CONTAINING VARIOUS CONCENTRATIONS OF LEO

| *Concn. of LEO M* | *Diffusion current constant* | | | | |
|---|---|---|---|---|---|
| | *Tl(I)* | *Pb(II)* | *Cd(II)* | *Zn(II)* | *Co(II)* |
| $2\cdot10^{-6}$ | 2.64 | 3·63 | 3·34 | 3·35 | 3·38 |
| $5\cdot10^{-6}$ | 2.65 | 3·59 | 3·31 | 3·36 | 3·35 |
| $1\cdot10^{-5}$ | 2.64 | 3·59 | 3·33 | 3·40 | 3·44 |
| $2\cdot10^{-5}$ | 2.66 | 3·59 | 3·39 | 3·45 | 3·49 |
| $5\cdot10^{-5}$ | 2.68 | 3·64 | 3·38 | a | a |
| $1\cdot10^{-4}$ | 2.70 | 3·61 | 3·36 | a | a |
| $2\cdot10^{-4}$ | 2.69 | 3·62 | 3·35 | a | a |
| $5\cdot10^{-4}$ | 2.69 | 3·61 | 3·39 | a | a |
| $1\cdot10^{-3}$ | 2.65 | 3·67 | 3·39 | a | a |
| Mean value | 2.67<br>$\pm.02_3$ | 3·62<br>$\pm.02_7$ | 3·36<br>$\pm.03_0$ | 3·39<br>$\pm.04_6$ | 3·41<br>$\pm.06_2$ |

[a] Can not be determined accurately because of the hydrogen wave.

TABLE VII

RELATION OF THE DIFFUSION CURRENT CONSTANT, *I*, AND THE RELATIVE VISCOSITY, $\eta_r$, OF 0.1*M* POTASSIUM NITRATE SOLUTION CONTAINING VARIOUS CONCENTRATIONS OF GELATIN

| *Concn. of gelatin %* | *Relative viscosity* ($\eta_r$) | $I\cdot\eta_r^{1/2}$ | | |
|---|---|---|---|---|
| | | *Pb(II)* | *Cd(II)* | *Zn(II)* |
| 0.001 | 1.002 | 3·56 | 3·32 | 3·33 |
| 0.02 | 1.010 | 3·52 | 3·33 | 3·39 |
| 0.05 | 1.022 | 3·49 | 3·24 | 3·34 |
| 0.1 | 1.047 | 3·21 | 3·28 | 3·36 |
| 0.2 | 1.090 | 3·05 | 3·19 | 3·28 |
| 0.4 | 1.188 | — | 3·14 | 3·27 |

diffusion of simple electrolytes[15]. In fact, the decrease of diffusion current constants with the increase of the concentration of gelatin can not be explained by the effect of viscosity of the solution (Table VII). It is plausible, therefore, that the effect of gelatin on the diffusion current constant is due to the interaction of reducible ions with gelatin molecules. Previous papers[3,6] indicate that the effect of gelatin on the diffusion current of lead ion becomes pronounced when the pH of the solution is larger than 4. In neutral solutions, imidazol and carboxyl groups of a gelatin molecule are dissociated and many metal ions are supposed to be chemically combined with these active groups. Furthermore, there is a possibility that electroactive species are physically adsorbed on macro-molecules such as gelatin[6]. These interactions between electroactive species and gelatin molecules clearly reduce the concentration of free electroactive species in the solution, and, thus, decrease their diffusion current constants. The effect of gelatin on the diffusion current constant of thallium(I) ion was shown to be negligible in comparison with that on lead(II), cadmium(II) and

*References p. 493*

cobalt(II) ions (Table V), which is in agreement with the well-known fact that the tendency of thallium(I) ion to make complex ions with complex-forming substances is usually very small. Table V also shows that the diffusion current constant of the lead acetate ion in the acetate buffer solution of pH 4.9 is kept approximately constant when the concentration of gelatin is increased. This might be explained by assuming that the presence of excess amounts of acetate ions, which easily react with lead ions to make lead acetate complex, prevents the relatively weak complex formation between lead(II) ions and gelatin molecules.

The discussion mentioned above is also confirmed by the experimental results of the effect of the concentration of lead(II) ions on the diffusion current in 0.1*M* potassium nitrate solution containing 0.2% gelatin (Fig. 3). If the decrease of the diffusion current constant of the lead (II) ion is due to the increase of the viscosity of the solution, the ratio of the diffusion current to the concentration of the lead(II) ion, $i_d/C$, must remain constant independent of the concentration of the lead(II) ion. Fig. 3 clearly indicates that the value of $i_d/C$ of the lead(II) ion gradually increases with the increase of the concentration of the lead(II) ion and reaches a constant value when the concentration of the lead(II) ion is higher than 1.5 m*M*. This can only be explained by assuming some kind of interaction between lead(II) ions and gelatin molecules.

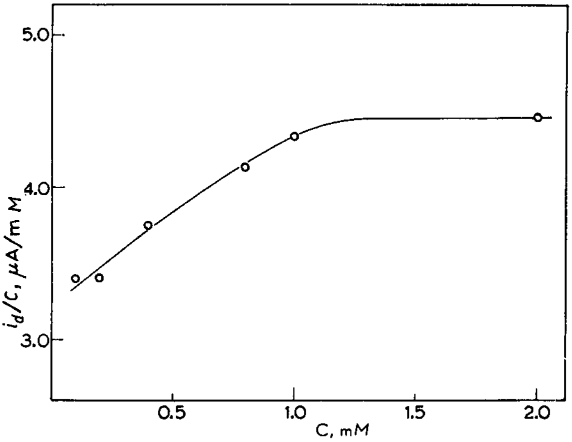

Fig. 3. Relation between $i_d/C$ of Pb(II) ion and the bulk concentration of Pb(II) ion, $C$, in 0.1*M* $KNO_3$ solution containing 0.2% gelatin.

In conclusion, it can be said that the addition of gelatin of relatively high concentration generally decreases diffusion current constants of many electroactive species because of the interaction between these electroactive species and gelatin molecules. In the polarographic analysis using a conventional DME, the concentration of gelatin as a maximum suppressor is usually less than 0.01%, where the effect of gelatin on the diffusion current constant is negligibly small. However, when the more sensitive methods, such as the use of the rotated dropping mercury electrode or the alternating current polarograph, are employed, this effect of gelatin will introduce some inevitable errors in the polarographic analysis.* By using LEO as a maximum suppressor instead of gelatin, a very good constancy of diffusion current constant is obtained in many cases. Furthermore, the solution of LEO is quite stable and completely free from deterioration. In these respects, the use of LEO as a maximum suppressor is much preferable to that of gelatin in the polarographic analysis.

## ACKNOWLEDGEMENT

The authors thank the Ministry of Education for the financial support granted for this research.

## SUMMARY

The effect of gelatin and LEO on diffusion current constants of some metal ions at the DME was investigated. LEO was shown to be very effective as a maximum suppressor, the MSP's of which were usually less than $1 \cdot 10^{-5} M$. Diffusion current constants were generally decreased by the addition of gelatin of relatively high concentration, mainly due to the interaction of electroactive species with gelatin molecules. It was found that diffusion current constants are unaffected by the addition of LEO over its wide concentration range. LEO has many advantages as a maximum suppressor, and the use of some kinds of synthetic detergents similar to LEO is strongly recommended in polarographic analysis of high sensitivity.

## RÉSUMÉ

On a examiné l'influence de la gélatine et de l'éther polyoxyéthylènelaurylique sur les constantes du courant de diffusion de quelques ions métalliques, à l'électrode à goutte de mercure. L'emploi de l'éther polyoxyéthylènelaurylique présente des avantages et il est recommandé en polarographie.

## ZUSAMMENFASSUNG

Es wurde der Einfluss von Gelatine und Lauryl-polyoxyäthylenäther auf die Konstanten der Diffusionsströme einiger Metallionen an der Quecksilbertropfelektrode untersucht. Lauryl-polyoxyäthylenäther verursacht keine Änderung der Konstanten und wird deshalb für polarographische Bestimmungen empfohlen.

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* The disadvantage of gelatin as a maximum suppressor in the polarographic analysis using a rotated dropping mercury electrode was recently pointed out by KOLTHOFF AND OKINAKA[4], when they recommended the use of polyacrylamide as a maximum suppressor.

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# POTENTIOMETRIC STUDIES ON COPPER FERROCYANIDE

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Several research workers have investigated the reaction between copper salts and potassium ferrocyanide, mostly by analytical methods but also by physico-chemical methods; there is, however, hardly any agreement between the views expressed by these authors.

RAUTER[1] was of the opinion that copper ferrocyanide adsorbed some potassium ferrocyanide and that the precipitate, owing to this colloidal nature, was peptised before it could be washed entirely free of potassium ferrocyanide; hence purely analytical methods could not be of much use in determining the composition of copper ferrocyanide. WYROUBOFF[2] reported the formation of three compounds under varying conditions corresponding to the formulae: $Cu_2[Fe(CN)_6]$, $K_2Cu[Fe(CN)_6]$, and $K_2Cu[Fe(CN)_6]\cdot K_4Fe(CN)_6$. MULLER, WEGELIN AND KELLERHOFF[3] studied the compositions of the precipitates formed by the interaction of copper sulphate with $K_4Fe(CN)_6$ and also with hydroferrocyanic acid and expressed the view that a precipitate of constant composition can only be obtained when one of the components is in large excess. They suggested the formula $K_2Cu_3[Fe(CN)_6]_2$ for the compound that is brown in colour and $K_2Cu[Fe(CN)_6]$ for the yellow compound.

WILLIAMS[4] reported the formation of $Cu_4K_4[Fe(CN)_6]_3$ by precipitating solutions of $K_4Fe(CN)_6$ with a cupric salt, and of $Cu_6K_8[Fe(CN)_6]_5$ by the exact precipitation of $K_4Fe(CN)_6$ solutions containing a large excess of KCl. Compounds of variable compositions, such as $Cu_7K_6[Fe(CN)_6]_5\cdot 22H_2O$; $Cu_9K_2[Fe(CN)_6]_5\cdot 50H_2O$, are reported to have been formed under different conditions.

KOLTHOFF[5] titrated copper salts conductometrically with $K_4Fe(CN)_6$ and observed that the normal salt $Cu_2[Fe(CN)_6]$ was first precipitated. With more ferrocyanide this salt formed the double salt $K_2Cu_3[Fe(CN)_6]_2$, and this was followed by a third inflexion point corresponding to the formation of $K_4Cu_4[Fe(CN)_6]_3$. BRITTON AND DODD[6] could not confirm the results of KOLTHOFF but obtained two inflexion points corresponding to the formation of $Cu_2[Fe(CN)_6]\cdot x\ K_4Fe(CN)_6$ where $x = 0.16$ and 0.40. BHATTACHARYA AND GAUR[7] studied the composition by applying physico-chemical methods and suggested that the compound formed is $K_2Cu[Fe(CN)_6]$, which in excess of copper sulphate changes to $K_2Cu_3[Fe(CN)_6]_2$.

In view of the conflicting opinions and in the absence of any decisive views on the composition of copper ferrocyanide, it was considered worthwhile to make a more comprehensive study of its composition by applying electrometric methods, since these give more conclusive results regarding the composition of complex metallic ferro and ferricyanides (R. S. SAXENA *et al.*[8]). In this paper only the results of potentiometric titrations have been included and discussed.

## EXPERIMENTAL

The $CuSO_4$ and $K_4Fe(CN)_6$ used were AnalaR (B.D.H.) chemicals. With various concentrations of the two salts in solution, potentiometric titrations were performed both by the direct and the reverse methods, *i.e.* by adding $K_4Fe(CN)_6$ solution from the micro-burette to the copper sulphate solution in the electrode cell and vice-versa. Potassium ferrocyanide solution containing 1% $K_3Fe(CN)_6$ was used to make the ferri–ferrocyanide electrode[9]. A bright platinum foil was dipped in the solution being titrated and used as an indicator electrode in conjunction with a saturated calomel electrode. The E.M.F. was measured on a Cambridge pH meter. The electrode cell was immersed in an electrically controlled thermostat to keep the temperature constant and the titration solution was stirred continuously by means of an electrically driven stirrer. The titrations were also carried out in the presence of alcohol and electrolytes such as $NH_4NO_3$, $(NH_4)_2SO_4$, $K_2SO_4$. Curves were plotted of the $E$(observed) *versus* the volume of the titrant added and from the sharp jump in potential shown on the titration curves, the equivalence point was found. This was further checked by calculating the maximum value of $dE/dC$ in each case. 20 ml of the reagent was taken in the cell each time.

TABLE I

SUMMARY OF RESULTS OF POTENTIOMETRIC TITRATIONS

| *$K_4Fe(CN)_6$ solution molarity* | *$CuSO_4$ solution molarity* | *Equivalence points ml of $K_4Fe(CN)_6$ or $CuSO_4$ required for the formation of $K_2Cu_3[Fe(CN)_6]_2$* | | | | | |
|---|---|---|---|---|---|---|---|
| | | *Calculated* | *Found experimentally from dE/dC in presence of* | | | | |
| | | | *Alcohol* | | *$NH_4NO_3$ 2 g* | *$(NH_4)_2SO_4$ 2 g* | *$K_2SO_4$ 2 g* |
| | | | 0% | 20% | | | |
| | | | *Direct titrations* (Figs. 1–4) | | | | |
| 1/10 | 1/20 | 6.66 | 6.55 | 6.65 | 6.75 | 6.60 | 6.65 |
| 1/20 | 1/100 | 2.66 | 2.60 | 2.68 | 2.70 | 2.68 | 2.65 |
| 1/50 | 1/200 | 3.33 | 3.30 | 3.35 | 3.40 | 3.36 | 3.34 |
| 1/150 | 1/400 | 5.0 | 5.0 | 5.05 | 5.05 | 5.10 | 4.95 |
| | | | *Reverse titrations* (Figs. 5–8) | | | | |
| 1/20 | 1/4 | 6.0 | 5.95 | 6.0 | 6.05 | 5.95 | 5.95 |
| 1/40 | 1/10 | 7.5 | 7.45 | 7.55 | 7.55 | 7.40 | 7.45 |
| 1/160 | 1/20 | 3.75 | 3.70 | 3.72 | 3.76 | 3.70 | 3.74 |
| 1/800 | 1/160 | 6.0 | 5.94 | 5.98 | 6.04 | 5.90 | 5.96 |

## DISCUSSION

From the strengths of the solutions of $K_4Fe(CN)_6$ ($M/10$) and $CuSO_4$ ($M/20$), the calculated equivalents for the formation of further probable compounds are given below.

1. Titration values for 20 ml of $M/20$ $CuSO_4$ soln. in direct titration:

| $K_2Cu[Fe(CN)_6]$; | $Cu_2[Fe(CN)_6]$; | $K_2Cu_3[Fe(CN)_6]_2$ | $K_4Cu_4[Fe(CN)_6]_3$ |
|---|---|---|---|
| 10.0 ml | 5.0 ml | 6.66 ml | 7.5 ml |

($M/10$ $K_4Fe(CN)_6$ solution)

2. Titration values for 20 ml of $M/20$ $K_4Fe(CN)_6$ solution in reverse titrations:

| | | | |
|---|---|---|---|
| 4.0 ml | 8.0 ml | 6.0 ml | 5.33 ml |

($M/4$ $CuSO_4$ solution)

The titration values required for the formation of the above compounds, employing different concentrations of reactants, can be calculated accordingly both in the case of direct and reverse titrations.

The potential of the ferricyanide–ferrocyanide electrode at 25° is given by:

$$E = E_0 + 0.059 \log [\mathrm{Fe(CN)_6}]^{-3} / [\mathrm{Fe(CN)_6}]^{-4}.$$

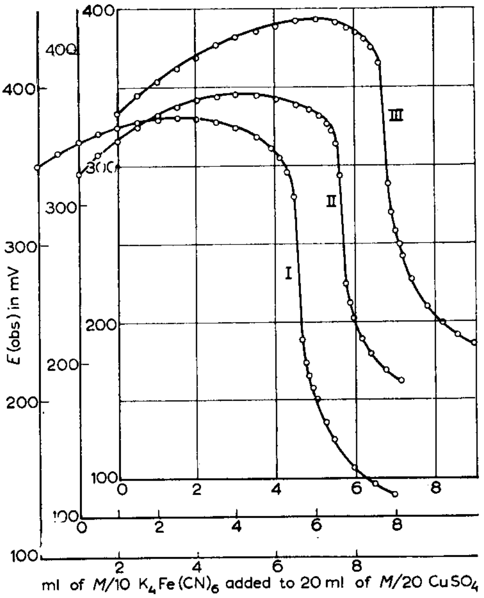

Fig. 1.

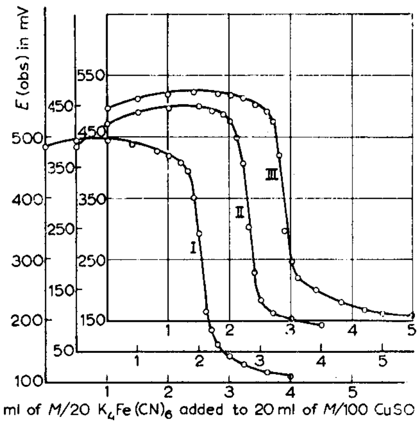

Fig. 2.

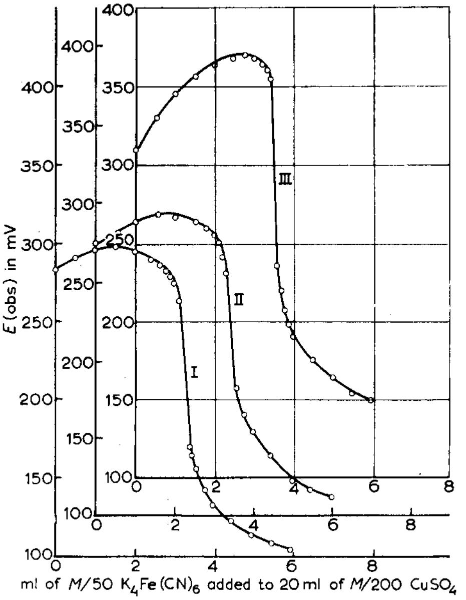

Fig. 3.

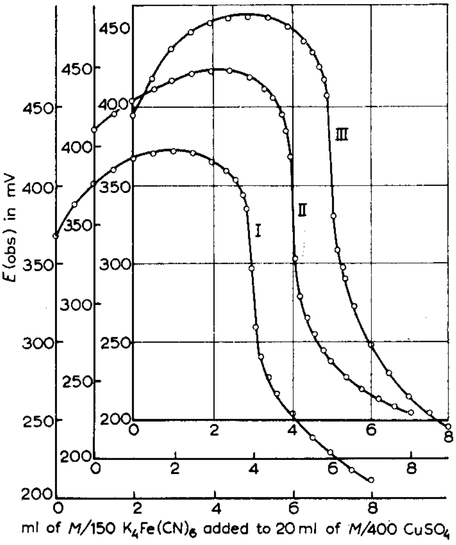

Fig. 4.

Figs. 1–4. Direct titrations. Curve I: 0% alcohol; curve II: 20% alcohol; curve III: 2 g $NH_4NO_3$.

*References p. 499*

When copper sulphate solution is titrated with potassium ferrocyanide solution containing a little ferricyanide solution, the ferrocyanide is removed until all the metal is precipitated. As long as the ferrocyanide ions are removed, the potential remains in the oxidising region, but as the first excess of ferrocyanide is added, a sharp change in the E.M.F. of the titration cell is observed at the equivalence point. In the reverse titrations (when $CuSO_4$ solution is added from the micro-burette to $K_4Fe(CN)_6$ in the cell) the ferrocyanide ions are removed from the solution by precipitation and the E.M.F. of the cell remains practically constant. But when the last traces of the ferrocyanide ions have been removed (*i.e.* in the vicinity of the end-point), a sharp upward jump in potential is observed indicating the end-point. The ferri–ferrocyanide electrode ceases to work after the equivalence point has been crossed and hence the E.M.F. assumes a practically constant value.

In the direct titration curves (Figs. 1–4), the E.M.F. at first slightly rises at the beginning of the reaction, then becomes practically constant and afterwards begins to decrease with a sharp fall in potential being observed at the end-point. In the reverse titrations (Figs. 5–8), however, the E.M.F. gradually increases from the start of the reaction, and a marked upward jump is obtained at the equivalence point after which the potential assumes a constant value. The potentiometric titration curves are regular in form.

It was observed that copper ferrocyanide, which is formed as a chocolate brown precipitate, is deposited on the platinum electrode, making it less sensitive. Under these conditions the results are irregular, it takes a long time for the potential to become constant and the titration curves are peculiar in shape. Hence care must be taken that the electrode is not entirely covered with the precipitate. Is is necessary that the platinum electrode should be cleaned with nitric acid after each titration, followed by rubbing with emery paper and igniting. Continuous stirring in the neighbourhood of the electrode has a favourable effect. The sharpness of the potential break and the accuracy of the end-point are dependent upon these precautions.

It is clear from Figs. 1–8 and the summary of results given in Table I that the reaction between $CuSO_4$ and $K_4Fe(CN)_6$ can be successfully followed potentiometrically using a ferri–ferrocyanide electrode, with either of the reactants used as the titrant. The point of equivalence obtained from the maximum $dE/dC$ and from the sharp inflexion in the curves, occurs at a stage where the molecular ratio of the reactants $K_4Fe(CN)_6$ and $CuSO_4$ is 2:3 corresponding to the formation of $K_2Cu_3[(Fe(CN)_6]_2$, and is very different from those required for the formation of other probable compounds $K_2Cu[Fe(CN)_6]$, $Cu_2[Fe(CN)_6]$, $K_4Cu_4[Fe(CN)_6]_3$ etc., as reported earlier in the literature. The curves have a regular form, a marked break in potential is observed at the end-point and the results are accurate and reproducible. In the presence of alcohol, no particular change in the nature of the curves or in the magnitude of the break in potential is obtained, except that the observed end-point is slightly nearer the calculated value (see Table I). This may be due to the decrease in solubility of copper ferrocyanide and also to suppression of the adsorption of the reacting ions by the precipitate in presence of alcohol. The addition of electrolytes such as $NH_4NO_3$, $(NH_4)_2SO_4$ and $K_2SO_4$, has practically no effect on the accuracy of the end-point and the nature of the curves but the magnitude of the break in potential increases when they are present.

Potentiometric titrations yield very accurate and reproducible results and afford a fairly good method for the quantitative determination of copper solutions. The titration is simple, rapid and accurate. The composition of copper ferrocyanide calculated from E.M.F. measurements is best represented by the molecular formula $K_2Cu_3[Fe(CN)_6]_2$.

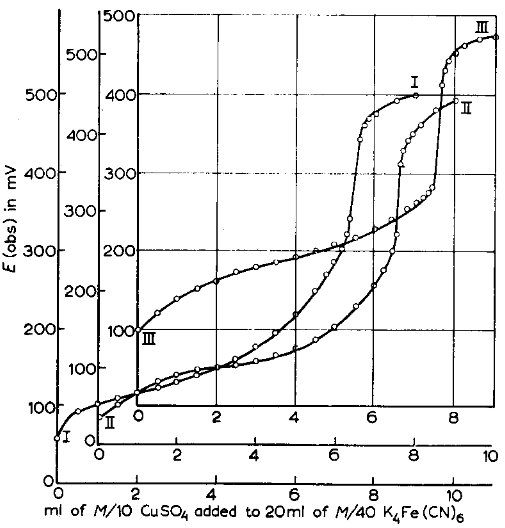

Fig. 5.

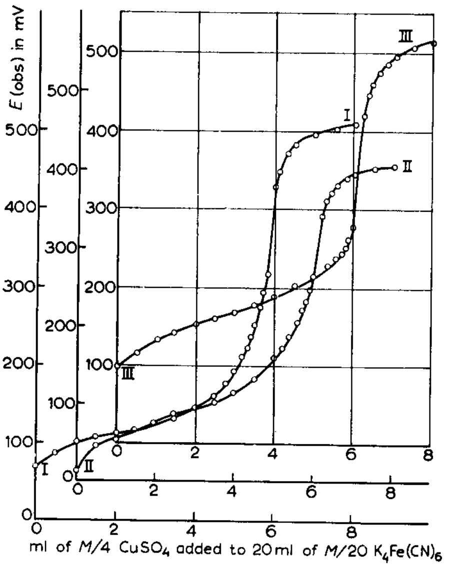

Fig. 6.

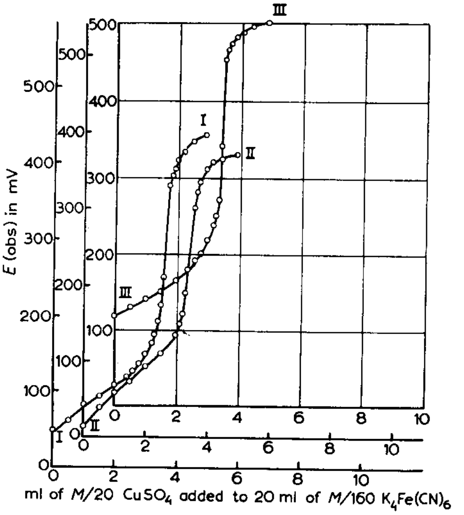

Fig. 7.

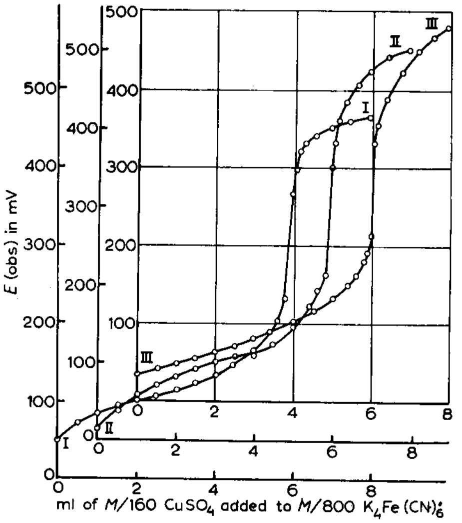

Fig. 8.

Figs. 5–8. Inverse titrations. Curve I: 0% alcohol; curve II: 20% alcohol; curve III: 2 g $NH_4NO_3$.

## SUMMARY

The formation and precipitation of copper ferrocyanide has been studied by potentiometric titrations of $CuSO_4$ and $K_4Fe(CN)_6$ at various concentrations using a ferricyanide-ferrocyanide electrode; each of the reactants was alternately used as the titrant. The end-point obtained from the maximum value of $dE/dC$ corresponds to the formation of a compound with the molecular formula $K_2Cu_3[Fe(CN)_6]_2$. The titration curves have a regular form, a sharp break in potential occurs at the end-point and the results are accurate and reproducible. The method is simple and rapid and offers a fairly accurate means of determining copper in solutions. The effects of ethanol and electrolytes such as $NH_4NO_3$, $(NH_4)_2SO_4$ and $K_2SO_4$ on the end-point as well as on the nature of the curves were investigated.

## RÉSUMÉ

La précipitation du ferrocyanure de cuivre a été étudiée par potentiométrie. On peut admettre la formation du composé $K_2Cu_3[Fe(CN)_6]_2$. Cette méthode simple et rapide permet le dosage du cuivre.

## ZUSAMMENFASSUNG

Der Verlauf der Niederschlagsbildung von Kupferferrocyanid wurde potentiometrisch verfolgt. Beim Endpunkt der Titration entspricht die Zusammensetzung des Niederschlages der Formel $K_2Cu_3[Fe(CN)_6]_2$. Die Methode erlaubt eine einfache und rasche Kupferbestimmung.

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## BUCHBESPRECHUNG

*Analyse der Fette und Fettprodukte einschl. der Wachse, Harze und verwandter Stoffe*, herausgegeben von H. P. Kaufmann, unter Mitwirkung namhafter Fachleute in 2 Bänden mit zus. 1860 S., Springer Verlag Berlin, Göttingen, Heidelberg, 1958, preis (beide Bände): DM 248.—.

Der erste Band (allgemeiner Teil) behandelt auf *ca.* 1100 Seiten die Chemie und Analyse der reinen Fette, deren Bausteine und Begleitstoffe (Sterine, Lipochrome, Phosphatide usw.) sowie die natürlichen Wachse und Harze als verwandte Stoffe. Die Zerlegung von Fettsäuregemischen und die Bestimmung der Einzelbestandteile wird sehr ausführlich beschrieben, wobei den physikalischen Methoden sehr viel Platz eingeräumt wird. Es braucht wohl nicht besonders hervorgehoben zu werden, dass alle modernen Methoden der Analyse und Trennung (z.B. mikro- und chromatographische Methoden) die ihnen gebührende Berücksichtigung erfahren haben.

Der zweite Band (spezieller Teil, *ca.* 650 Seiten) beschreibt die mikroskopische Untersuchung der fettliefernden Rohstoffe, die Analyse der Nahrungsfette, Milcherzeugnisse und Kakaofette einschliesslich der Methoden zur Bestimmung der Verdorbenheit von Fetten. Der grössere Teil dieses Bandes befasst sich mit den Untersuchungsmethoden der technisch wichtigen Fette, Fettprodukte und verwandten Stoffen (Textil-Öle, Seifen, wasch-aktive Stoffe, sulfonierte Öle und Fette, Anstrichmittel, Faktis, Lederfettungsmittel, Wollfett, Glycerin und andere Polyalkohole).

Dieses Werk, aus der Hand des sehr bekannten Fachmannes unter Mitarbeit zahlreicher anderer Fachleute, füllt zweifellos eine lang empfundene Lücke in der chemischen Fachliteratur aus. Wer sich mit der Untersuchung von Fettprodukten, besonders auf dem technischen Sektor, zu befassen hat, wird das Erscheinen dieses ausgezeichneten Buches sehr begrüssen. Durch die Beschreibung der Trennungs- und Analysenmethoden für kleinste Substanzmengen wird aber auch der auf biologischem oder physiologischem Gebiet arbeitende Wissenschaftler das Werk als unentbehrlich betrachten. Bei den technischen Produkten sind, ihrer Bedeutung entsprechend, die Analysenmethoden für synthetische Waschmittel und Anstrichstoffe sehr ausführlich behandelt. Die Analytik der Anstrichmittel umfasst u.a. Nachweis- und Bestimmungsmethoden der einzelnen Kunstharze, wodurch dieses Kapitel auch für die Untersuchung von Kunststoffen wertvolle Hinweise gibt. Der Titel des Werkes ist vielleicht etwas irreführend, da man vermuten könnte, es handle sich um eine Sammlung von Analysenvorschriften für Fette und verwandte Produkte. In Wirklichkeit ist der Charakter des Werkes mehr der eines Handbuches der Fettchemie und verwandter Gebiete, denn auch der Wissenschaftler, der sich mit Fragen der Synthese, Strukturermittlung und anderen Problemen dieser Körperklasse abgibt, die mit der Analyse direkt nichts zu tun haben, wird mit Vorteil dieses Werk zu Rate ziehen.

K. EDER (Genève)

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# Announcement

## CHROMATOGRAPHIE DES GAZ — GROUPE DE STANDARDISATION

Sous l'égide de la section de Chimie Analytique de l'Union Internationale de Chimie Pure et Appliquée, un groupe a été constitué en vue de présenter au Conseil de l'Union des propositions concernant la *standardisation de la nomenclature et de la présentation des données de Chromatographie des gaz.*

Ce groupe est présidé par Mr. D. AMBROSE (National Chemical Laboratory, Teddington, G.B.). Il comprend Messieurs: Dr. A. T. JAMES (Grande Bretagne), Prof. Dr. A. I. M. KEULEMANS (Pays-Bas), Dr. E. KOVATS (Suisse), Dr. R. RÖCK (Allemagne), Dr. F. H. STROSS (U.S.A.) et C. ROUIT, Ing. Dr. (France).

Le travail actuel du groupe consiste à mettre au point un document basé sur deux articles parus dans *Anal. Chem.*, 30, Nr. 10 (octobre 1958) 1582: Presentation of Gas-Liquid Chromatographic Retention Data, par D. AMBROSE, A. I. M. KEULEMANS ET J. H. PURNELL.

*Anal. Chem.* 30, Nr. 10 (octobre 1958) 1586: Terms and units in gas chromatography, par H. W. JOHNSON ET F. H. STROSS.

En vue de rendre aussi ouverte et aussi large que possible la discussion qui conduira à la publication du document envisagé, toutes les personnes qui utilisent la chromatographie des gaz ou travaillent à en développer les théories et les applications sont invitées à collaborer avec le groupe.

A cet effet, leurs remarques, critiques, suggestions ou approbations concernant les données des publications sous référence pourraient être adressées à:

Monsieur CHARLES ROUIT, Chef du Département Laboratoires, Raffinerie de la Société Française des Pétroles BP, Lavéra-Martigues (Bouches-du-Rhône).

L'étape initiale conduira à un document en anglais. Un document identique en français est en préparation et sera proposé en temps utile pour discussion aux intéressés.

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