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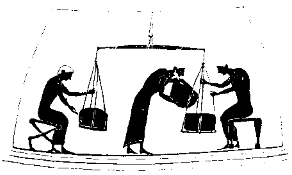

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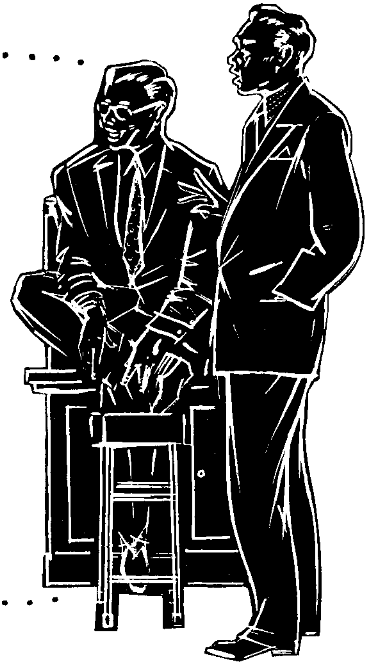

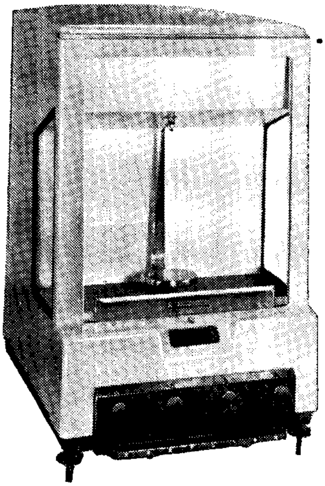

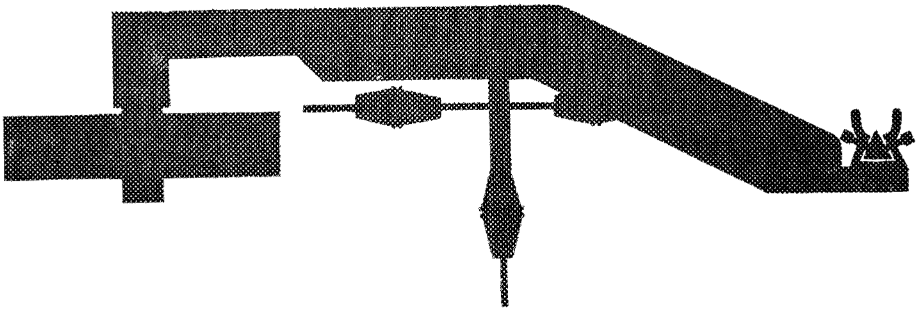

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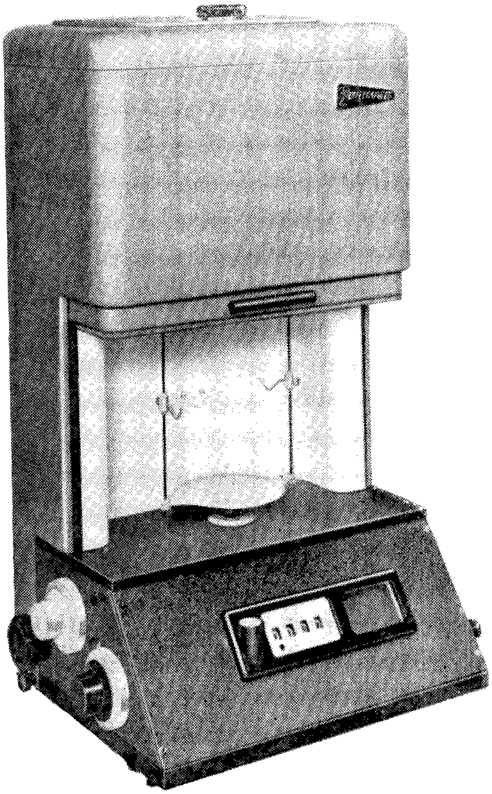

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THE MICRO-KJELDAHL DETERMINATION OF NITROGEN

AN INVESTIGATION OF THE EFFECTS OF ADDED SALT AND CATALYSTS

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Summary—An examination has been made of the effects of concentration of potassium sulphate and of 21 single and mixed catalysts on the recovery of nitrogen by the Kjeldahl method. Mercury has been confirmed as the best catalyst, and a higher concentration of potassium sulphate than usual is recommended. Observations are made on various factors, including the "clearing time", which affect the determination.

INTRODUCTION

In spite of the widespread use of the Kjeldahl method for the determination of nitrogen, no one has yet undertaken a comprehensive comparison of a number of catalysts under varying conditions. Previous investigators have either investigated different catalysts under one set of conditions only, or have varied the conditions, but with only one or two catalysts. In many cases the test substances used have been simple amino compounds, which would not be expected to give any difficulty, whatever modification was used. In some cases, non-nitrogenous test substances were used to investigate "clearing times", but no attempt was made to demonstrate that the proposed conditions would lead to quantitative recovery of nitrogen from a nitrogenous sample.

In the present work, the behaviour of different catalysts at varying salt concentrations has been investigated. The boiling points of solutions of varying concentrations of added salt have also been determined.

THE INFLUENCE OF TEMPERATURE ON THE DIGESTION

The addition of potassium sulphate was first suggested by Gunning,[1] who recommended the use of "one part of salt to two parts of acid", *i.e.* 0·9 g of salt to 1·0 ml of acid. Later, Hibbard[2] and Self[3] found that a loss of ammonia could occur if the salt concentration became excessive, but many workers apparently did not appreciate that the excessive concentrations referred to involved about 2 to 3 g of potassium sulphate to 1 ml of sulphuric acid, and in consequence used absurdly small concentrations of salt; as low as 0·1g to 1ml of acid. In fact, recent work[4,5] has shown that as much as 1·0 g of salt to 1·0 ml of acid may safely be used.

Gunning thought that the addition of potassium sulphate, giving potassium hydrogen sulphate in solution, would lead to the loss of water rather than sulphur trioxide on heating, and hence a stronger acid would be formed, which would speed the digestion of the sample. Whether or not this is true, it is generally agreed nowadays that the primary function of the salt is to raise the boiling point of the mixture (which will have the same effect of speeding the digestion).

Only six previous investigations have been made of the boiling points at varying salt concentrations, and only one of these has gone above 1·0 g/ml concentration. This work is summarised in Table I (in some cases, the figures given have been estimated from the original author's graph).

These results, and possible reasons for the discrepancies, will be discussed later, in conjunction with the results of the present investigation.

TABLE I—BOILING POINTS (°C) OF SOLUTIONS OF POTASSIUM SULPHATE IN SULPHURIC ACID

Concn. of K_2SO_4, *g/ml*	Snyder and Coleman[6]	Ogg and Willits[7]	Middleton and Stuckey[8]	Lake *et al.*[9]	McKenzie and Wallace[5]	Bradstreet[10]
0	345	—	328	—	—	322*
0·25	350	332	336	—	—	329
0·33	—	—	339	—	344	333
0·5	356	342	347	362	—	339
0·67	—	—	—	367	361	346
0·75	372	354	359	371	—	349
1·00	—	—	371	382	380	—
1·33	—	—	—	—	397	—
1·67	—	—	—	—	418	—
2·00	—	—		—	406†	—

* at 0·08 g/ml

† This value is probably erroneous[11]

EXPERIMENTAL

The present measurements were carried out using a thermometer (in about 10 ml of solution) and a small copper-constantan thermocouple (in about 1·5 ml of solution).

Use of a thermometer

A 0–500° mercury thermometer was used. Calibration with naphthalene and benzophenone (recommended[12] as secondary fixed points) showed that it was accurate at 218° and 2° low at 306°. For the present purpose it was considered sufficient to apply a 2° correction to readings between 300° and 400°. Determinations were then carried out on boiling solutions of potassium sulphate in sulphuric acid, contained in a "30-ml" Kjeldahl flask. In each case the bulb of the thermometer was immersed in the liquid, and about 6 in. of stem were in the vapour. The solutions were boiled vigorously so that acid just distilled from the neck of the flask, and the maximum steady boiling point was noted. The results obtained are shown in Table II.

TABLE II—BOILING POINTS OBTAINED WITH THERMOMETER

K_2SO_4, *g*	H_2SO_4, *ml*	Concentration, *g/ml*	Corrected b.p., °*C*
0	10	0	329
5	10	0·5	344
7	7	1·0	365
9	6	1·5	388
10	5	2·0	410

Use of a thermocouple

This was made from fine wires, and enclosed in a thin glass sheath. It was calibrated at seven points up to 400° in the following manner.

At the ice point both the hot and cold junctions were immersed in a beaker of melting ice and the millivoltmeter adjusted to zero. Measurements were then taken at the boiling points of water, bromobenzene, naphthalene, diphenyl and benzophenone, and at the melting point of potassium dichromate, using for this last point a furnace similar to that recommended.[12]

From these figures a calibration curve was obtained which was slightly curved between 0 and 200° but linear from 200–400°.

Using this calibration, the boiling point of 10 ml of sulphuric acid was found to be 330°. When only 1·5 ml was used, the boiling point was less stable, and fluctuated between 328° and 330°. For subsequent work, using 1·5 ml of acid, 30-ml Kjeldahl flasks and a gas-heated rack were used. In each determination the mixture of acid and salt was heated gently over a low gas flame for 2 or 3 min to dissolve most of the solid, then the flame was increased.

The results obtained are shown in Table III.

TABLE III—BOILING POINTS OBTAINED WITH THERMOCOUPLE

Expt.	H_2SO_4, *ml*	K_2SO_4, *g*	Conc., *g/ml*	B.p., *°C*	Remarks
1	1·5	—	—	329	
2	1·5	0·75	0·5	344 ± 1	Maximum value attained in 5 min from start of ebullition. Constant for further 15 min.
3	1·5	1·5	1·0	364 ± 2	Attained in 8 min. Slight overall rise (362–365°) during succeeding 20 min.
4	1·5	2·25	1·5	387	Steady for 10 min.
5	1·5	3·0	2·0	404	Attained in 9 min, rising to 407° during further 25 min.
6	Solid $KHSO_4$		[≡ 3·3]		Evolution of bubbles at *ca.* 320°; steady temperature rise to >415°. No steady boiling point.

Although, as shown in Table III, the rise in temperature during digestion for about 20 min was not serious, it was thought desirable to find directly, by titration, if there was a significant loss of acid. Accordingly, the residual solutions from experiments 1, 3 and 5 in Table III were diluted to 500 ml, and aliquots titrated against 0·1*N* sodium hydroxide. The results were as follows:

Solution 1 contained 2·69 g of sulphuric acid
Solution 3 contained 2·70 g of sulphuric acid
Solution 5 contained 2·70 g of sulphuric acid
1·5 ml of sulphuric acid, not boiled, contained 2·74 g (theoretical = 2·71 g).

The discrepancy between the theoretical and observed values is probably due to inaccuracies in pipetting such a viscous liquid. Nevertheless, the apparent loss of acid on digestion (0·04 g) would only be sufficient to raise the boiling point by less than 1°, and consequently the loss of acid by evaporation is negligible under these conditions.

The boiling points obtained by the two methods, shown in Table IV, are thus in satisfactory agreement.

TABLE IV.—RESULTS OBTAINED BY THE TWO METHODS

K_2SO_4 concentration, *g/ml*	0	0·5	1·0	1·5	2·0
B.p. with thermometer, °*C*	329	344	365	388	410
B.p. with thermocouple, °*C*	329	344	364	387	405

DISCUSSION OF RESULTS

There is a considerable discrepancy in the literature over the boiling point of sulphuric acid alone. The approximately 98·4% acid is a constant boiling mixture, usually said to boil between 328–330°, but textbook values as far apart as 317°[13] and 338°[14] have been found. Recently, however, Kunzler,[15] in connection with the preparation of pure sulphuric acid, has stated that the boiling point of constant boiling acid (98·5%) is "nearly 330° at one atmosphere", and this figure has been confirmed in the present work. Neither Snyder and Coleman[6] nor Bradstreet,[10] however, whose results are quoted in Table I, commented on their figures of 345° and less than 322° respectively.

The figures of Lake *et al.*[9] appear somewhat high, but their values were recorded after boiling for 1 hr, during which time considerable evaporation could have occurred. They do not give a figure for sulphuric acid alone.

Our figures are in agreement with those of Ogg and Willits,[7] and Middleton and Stuckey,[8] but those of McKenzie and Wallace,[5] the only other workers to report comparable figures, are somewhat higher. Moreover, a graph of boiling point against concentration for their results shows a steeper slope than for those of other workers. Two reasons can be advanced for this. McKenzie[11] has stated that the intensity of heating used by him was greater than that used by us, which would lead to more rapid evaporation of acid, and hence a higher temperature. This effect would increase with increasing concentration. The second reason, apparently hitherto overlooked, is related to the amount of acid in the vapour phase, and distributed round the walls of the vessel. If the mixture is barely boiling, there will be very little acid in the vapour phase, and the concentration of the mixture will approximate to that calculated, but if boiling is vigorous, the amount of acid in the vapour phase will be greater, the interior of the vessel will be covered with a film of condensing acid, and the boiling solution at the bottom of the flask will, in consequence, be more concentrated. The effect will of course be more marked when "micro" quantities are used.

The effect on the boiling point of other substances present during digestion

The consumption of acid during digestion of an organic sample is greatest for fat, and is then about 10 ml of acid for 1 g of sample, or 0·05 ml for 5 mg. (Middleton and Stuckey[8] give the acid consumption for a number of compounds and molecular fragments). Using 1·5 ml of acid, a 5-mg sample would have the effect of raising an initial salt concentration of 1·0 g/ml to 1·035 g/ml which would raise the temperature by only about 1·5°.

Similarly, the presence of about 50 mg of catalyst would raise the boiling point only to a similar extent, and hence these factors may be ignored on the micro-scale.

The effect on the boiling point of variations in atmospheric pressure

The work of Lake *et al.*[9] indicates that the boiling point changes by about 15° for a pressure change of 175 mm of Hg. Variations in normal atmospheric pressure (740–770 mm) will therefore affect the boiling point by not more than 2–3°.

The effect of replacing potassium sulphate by sodium sulphate

Sodium sulphate, having a smaller molecular weight, might be expected to give a greater boiling point elevation than potassium sulphate, but the contrary has been reported,[5,8] and this unexpected finding has been confirmed in the present work. At a concentration of 1·0 g/ml, a solution of sodium sulphate gave a boiling point 7° lower than that of potassium sulphate.

THE INFLUENCE OF DIFFERENT CATALYSTS ON THE DIGESTION

The use of catalysts was first suggested by Wilfarth.[16] He investigated mercury, copper, iron, tin, manganese, bismuth and lead, and found their relative efficiency to be in the order shown. Mercury, however, led to difficulty at the distillation stage, because of formation of non-volatile ammines, and he therefore preferred to use copper, but later in the same year,[17] he showed how the ammines could very easily be broken down by the addition of potassium sulphide.

Subsequent work has confirmed the superiority of mercury (Phelps and Daudt[18] found it to be superior to 9 other elements, and Osborn and Wilkie[19] found it to be superior to 38 other elements) and it is therefore surprising that many analysts still prefer to use copper.

The only other single catalyst to gain widespread popularity is selenium, proposed by Lauro.[20] There has, however, been considerable controversy about the possible loss of ammonia when using this catalyst. Mixtures are frequently used; the most popular is a mixture of mercury and selenium, first suggested by Beet,[21] although here again a loss of ammonia has been alleged under certain conditions.

In the present work, the effects studied were (*a*) variation in the catalyst (15 single catalysts and 6 mixtures were used), (*b*) variation in the potassium sulphate concentration, and (*c*) variation in the type of sample (ammonium sulphate, benzylisothiouronium chloride, and nicotinic acid were used, typifying a simple ammonium salt, an easily digested compound, and a "refractory" compound).

The effect of variation in time was not studied, and a standard digestion time of 20 min was adopted. By comparing the results obtained with the three test samples, it could easily be seen whether the low results obtained under certain conditions were due to incomplete digestion or to decomposition of ammonia.

The effect of variation in the amount of each catalyst was not studied (the effect of a true catalyst should be independent of the amount, but this is probably not true in the present case). It was originally intended to use 0·2 mg mol of each catalyst (*e.g.* about 40 mg of HgO or 20 mg of Se, as commonly used), but it was soon apparent that this would lead to inconsistencies, and with the exception of a few of the early experiments, approximately equal amounts (20–30 mg) of each catalyst were used.

EXPERIMENTAL

Reagents

Sulphuric acid: Concentrated M.A.R.
Potassium sulphate: M.A.R.

Catalysts: The substances used were HgO, Se, H_2SeO_3, H_2SeO_4, $CuSO_4$, TiO_2, $FeCl_3$, $FeSO_4$, $Fe_2(SO_4)_3$, H_2PtCl_6, MoO_3, V_2O_5, $VOSO_4$, CrO_3, and Te. The best available commercial grade of each was used.

Ammonium sulphate: AnalaR.

Alkaline thiosulphate: 40% NaOH (w/v), containing 5% w/v $Na_2S_2O_3$.

Boric acid: AnalaR, 2% w/v in boiled-out distilled water.

Screened indicator: 2 vol. of 0·05% ethanolic methyl red + 1 vol. of 0·05% ethanolic methylene blue. (This has been found[22] to be superior to any other mixture of these components.)

Hydrochloric acid: standard 0·01*N* solution.

Procedure

About 5 mg of the test substance was weighed into a 30-ml Kjeldahl flask. The required weights of catalyst and potassium sulphate were added, followed by 1·5 ml of sulphuric acid. Each batch consisted of 5 such samples and one blank (containing sulphuric acid and potassium sulphate only). The 6 flasks were heated gently for 2–3 min, to dissolve most of the salt, then at full heat for 20 min.

After digestion, the flasks were allowed to cool. The contents were diluted with about 10 ml of water, and gently warmed if necessary to dissolve the "cake" of potassium hydrogen sulphate.

The contents of each flask, in turn, were then transferred to a distillation apparatus, and 10 ml of alkaline thiosulphate added (the addition of thiosulphate to the alkali is necessary only if mercury is used as a catalyst, but to avoid variation it was used throughout). The ammonia was then steam-distilled into 5 ml of boric acid, containing 4 drops of screened indicator. Distillation was allowed to proceed, at 4–5 ml/min, for 3 min with the tip of the condenser immersed in the boric acid, and a further 1 min with the tip clear of the surface. The end of the condenser was then washed down with water, and the contents of the receiver titrated against standard 0·01*N* hydrochloric acid.

DISCUSSION OF RESULTS

The results obtained are shown in Tables V–VII. Since several of the catalysts used affect both the rate of digestion and the loss of ammonia, it is more convenient to consider these two effects together. The question of the "clearing time" will be considered separately.

Using no catalyst, the recovery from ammonium sulphate was quantitative up to 440°, but the result of 17·6% obtained after a 20-min digestion with a mixture equivalent to potassium hydrogen sulphate shows that there is no "instantaneous" loss of ammonia at this salt concentration.

The results with benzylisothiouronium chloride were similar, and it thus appears that the maximum safe digestion temperature, using no catalyst, is about 430°. At this temperature, however, digestion of nicotinic acid was not quite complete.

Single catalysts

Mercury This catalyst had no apparent effect on the decomposition of ammonia, but a marked effect on the digestion of nicotinic acid, the recovery from which was satisfactory above 387°.

Selenium Elementary selenium caused decomposition of ammonia above about 387°. The recoveries from nicotinic acid were unsatisfactory, and hence selenium appears inferior to mercury in both these respects.

Experiments with selenious and selenic acids (*cf.* ref. 23) showed that the decomposition of ammonia was moderate with selenious acid, but very great with selenic acid. This effect, however, was not obvious with nicotinic acid, and it is likely that the reduction of selenate to selenite takes place more quickly than the digestion of nicotinic acid.

TABLE V—NITROGEN FOUND IN AMMONIUM SULPHATE
(Theoretical = 21·2% N)

K_2SO_4 concentration, *g/ml*		0	0·5	1·0	1·5	2·0	2·25	2·5	2·75	3·0	3·3
Temperature (from Table IV), °*C*		329	344	365	387	408	420*	430*	440*	450*	
Catalyst	Amount, *mg*										
None	—	—	—	—	—	21·3	—	20·9	21·3	16·8 18·0	17·6
HgO	40	—	—	—	21·2	21·3	—	21·2	21·2	19·0 12·8	—
Se	20	—	—	21·1	21·4	20·5	—	17·7	—	—	—
H_2SeO_3	25	—	—	21·3	20·9	19·3	—	—	—	—	—
H_2SeO_4	30	20·5	18·8	4·5	—	1·6	—	—	—	—	—
$CuSO_4$	75	—	—	—	—	21·1	19·6	18·7	—	—	—
TiO_2	20	—	—	—	—	21·3	—	20·7	—	—	—
$FeCl_3$	30	—	—	—	—	21·1	—	20·6	—	—	—
$FeSO_4$	30	—	—	—	—	21·2	—	20·5	—	—	—
$Fe_2(SO_4)_3$	30	—	—	—	—	21·2	—	—	—	—	—
H_2PtCl_6	80	—	—	nil	—	—	—	—	—	—	—
MoO_3	30	—	—	21·4	20·8	20·0	—	20·0	—	—	—
V_2O_5	20	20·8	20·3	19·0	18·2	15·2	—	—	—	—	—
$VOSO_4$	30	—	—	21·1	—	19·3	—	—	—	—	—
CrO_3	20	—	—	10·7	—	9·5	—	—	—	—	—
Te	25	—	—	—	—	21·1	—	19·9	—	—	—
HgO + Se	40/20	—	—	21·1	20·0	12·5	—	—	—	—	—
HgO + $CuSO_4$	40/20	—	—	—	21·3	20·9	—	20·8	—	—	—
Se + $CuSO_4$	20/20	—	—	—	21·2	20·5	—	—	—	—	—
HgO + Se + $CuSO_4$	40/20/20	—	—	21·0	19·7	17·7	—	—	—	—	—
V_2O_5 + Se	20/20	—	—	21·3	21·2	20·1	—	15·8	—	—	—
HgO + Te	40/20	—	—	—	21·2	21·0	—	20·6	—	—	—

* Extrapolated from a graph of the figures in Table IV

Copper This led to a loss of ammonia above 408°, and the recoveries from nicotinic acid were unsatisfactory.

Titanium This has never been recommended for routine use, but was briefly investigated in view of its high placing (fourth) in the list of Osborn and Wilkie.[19] It was found that loss of ammonia only occurred above 408°, and recovery of nitrogen from nicotinic acid was satisfactory only at this temperature.

Iron In view of somewhat conflicting statements in the literature iron was investigated as iron^{III} sulphate, iron^{III} chloride and iron^{II} sulphate. The mixture containing iron^{III} sulphate gave a cloudy suspension at once; that with iron^{III} chloride went cloudy almost at once, and that with iron^{II} sulphate gave an initially clear solution, which rapidly turned yellow, then cloudy, presumably due to oxidation followed by crystallisation of iron^{III} sulphate. The appearance at this stage was the same in all three cases; namely, a white precipitate in a yellow solution (the colour was discharged on cooling). It is apparent that, contrary to Stubblefield and De

TABLE VI—NITROGEN FOUND IN BENZYLISOTHIOURONIUM CHLORIDE
(Theoretical = 13·8% N)

K_2SO_4 concentration, *g/ml*	1·0	1·5	2·0	2·5	3·0
Temperature (from Table IV), °*C*	365	387	408	430*	450*
Catalyst					
None	—	—	13·8	14·0	13·5
HgO	—	—	13·9	13·4	13·6
Se	—	13·9	12·4	—	—
H_2SeO_3	—	13·6	13·1	—	—
H_2SeO_4	—	6·9	—	—	—
$CuSO_4$	—	—	13·8	13·4	—
TiO_2	—	—	14·0	—	—
$FeSO_4$	—	—	14·0	13·7	—
$Fe_2(SO_4)_3$	—	—	13·7	13·5	—
MoO_3	—	—	13·4	—	—
V_2O_5	—	13·9	13·0	13·2	—
$VOSO_4$	—	13·8	13·3	13·2	—
Te	—	—	13·8	13·6	—
HgO + Se	13·7	13·7	9·1	—	—
HgO + $CuSO_4$	—	13·9	13·8	—	—
Se + $CuSO_4$	13·7	13·5	11·4	—	—
HgO + Se + $CuSO_4$	13·8	11·3	7·3	—	—
V_2O_5 + Se	—	—	13·6	6·8	—
HgO + Te	—	—	13·7	13·2	—

* See footnote to Table V

Turk,[24] iron^{III} sulphate is not completely insoluble in boiling sulphuric acid. Bradstreet,[25] who recommended the use of iron^{II} sulphate did not comment on the precipitation of iron^{III} sulphate. The precipitate did appear to make boiling more regular.

As anticipated from these observations, the results were substantially the same for all three compounds. Loss of ammonia was evident above 408°, and recovery from nicotinic acid was quantitative only at this temperature.

Platinum This was claimed to be a satisfactory catalyst by Ulsch,[26] but later work[19] indicated a considerable loss of ammonia. In the present work one experiment led to complete loss of ammonia, and it was not further investigated.

Molybdenum, Vanadium, and Chromium The use of molybdenum or vanadium both led to loss of ammonia, vanadium pentoxide being worse than vanadyl sulphate in this respect. No great catalytic activity was apparent, and it is likely that the oxides are oxidants rather than catalysts. To support this view, chromium trioxide was briefly investigated. This led to considerable loss of ammonia.

Tellurium This has been claimed[27] to be less efficient than selenium, but not to cause loss of ammonia, and this is borne out by the present results.

Mixed catalysts

Mercury and selenium This mixture causes decomposition of ammonia at a lower temperature than either component alone. The maximum recovery of nitrogen

TABLE VII—NITROGEN FOUND IN NICOTINIC ACID
(Theoretical = 11·4% N)

K_2SO_4 concentration, *g/ml*	1·0	1·5	2·0	2·5
Temperature (from Table IV), °*C*	365	387	408	430*
Catalyst				
None	2·2	—	7·1	10·9
HgO	10·6	11·3	11·2	11·1
Se	8·6	9·0	10·9	9·1
H_2SeO_3	6·3	10·6	10·5	10·1
H_2SeO_4	9·0	10·6	10·9	6·6
$CuSO_4$	8·9	—	9·3	—
TiO_2	6·8	—	11·3	—
$FeSO_4$	3·1	—	11·3	—
MoO_3	4·5	—	—	—
V_2O_5	7·5	—	—	—
$VOSO_4$	4·1	—	—	—
Te	3·5	8·8	10·6	—
HgO + Se	11·1	10·6	6·0	—
HgO + Cu	10·1	—	—	—
Se + $CuSO_4$	7·5	—	—	—
HgO + Se + $CuSO_4$	11·0	—	—	—
V_2O_5 + Se	10·4	10·8	9·9	—
HgO + Te	10·8	11·3	11·2	10·9

* See footnote to Table V

from nicotinic acid occurs at a lower temperature, but if this temperature is exceeded decomposition of ammonia again occurs.

Mercury and copper Paul and Berry[28] concluded that this mixture is not more effective than mercury alone and the present work supports this conclusion.

Selenium and copper; mercury and selenium and copper These mixtures behaved similarly to selenium, and mercury and selenium respectively. In the light of the results with mercury and copper this is not unexpected. It is significant that none of the workers[29–31] who have recommended the ternary mixture have given good evidence of its superiority. Poe and Nalder[30] claimed it to be better than mercury or copper alone, but did not compare it with a mixture of mercury and selenium, and in any case, only analysed simple amino compounds.

Vanadium and selenium This mixture, originally recommended by Crossley,[32] led to a loss of ammonia above 387°. The recoveries from nicotinic acid were higher than with either component alone but still not satisfactory.

Mercury and tellurium As tellurium alone was shown to cause no significant loss of ammonia it was hoped that this mixture might prove an attractive substitute for mercury and selenium. The results show that this is the case, but there is no apparent improvement over the use of mercury alone. Since, however, the "clearing times" for the mixture were somewhat shorter than for mercury alone, it was thought desirable to compare these two catalysts more closely, by determination of the rate of digestion of nicotinic acid, using 1·5 ml of sulphuric acid and 2·25 g of potassium sulphate. The results, in Table VIII, show no significant difference.

TABLE VIII—COMPARISON OF MERCURY AND MERCURY-TELLURIUM CATALYSTS WITH RESPECT TO THE DIGESTION OF NICOTINIC ACID

Digestion time, *min*	Catalyst	
	Hg	Hg + Te
5	4·0%N	3·1%N
10	9·4	9·1
15	11·3	11·3
20	11·3	11·4

Amount of catalyst

A series of digestions of nicotinic acid was carried out, using 1·5 ml of sulphuric acid and 2·25 g of potassium sulphate, to determine the minimum amount of catalyst necessary. The results in Table IX show that 10 mg is adequate, and the use of 20 mg should provide an adequate margin of safety.

CONCLUSIONS

The results show clearly that none of the catalysts investigated is demonstrably superior to mercury, used alone, and it appears that there is no longer any justification for the use of any of the other catalysts mentioned.

THE "CLEARING TIME"

This, the time taken for the digest to become clear, has been widely used as a measure of the efficiency of the procedure. Clearing will obviously occur when all of the charred organic matter has been completely oxidised, but it does not necessarily follow that the conversion of nitrogen to ammonia will take place concurrently. Ashton,[33] for example, stated that clearing is no criterion of the completeness of digestion, and found that maximum recoveries of nitrogen were obtained 2–3 hr after clearing. His conclusions were supported by Dalrymple and King.[34] Similarly, Beet and Furzey[35] found that the use of copper sulphate as a catalyst gave results that were 2% low, unless an "afterboil" was given, and most published methods include a statement of the type "boil for 1 hr after clearing". On the other hand, Perrin[36] concluded that under the conditions used by him the conversions of nitrogen to ammonia and carbon to carbon dioxide occurred simultaneously, and no "afterboil" was needed. In general, however, it seems likely that these reactions will proceed

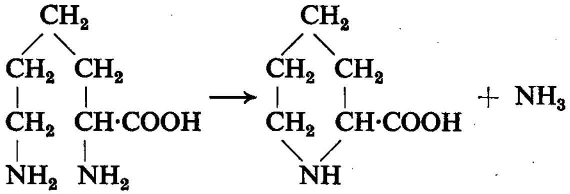
TABLE IX—EFFECT OF VARIATION IN THE AMOUNT OF MERCURY^{II} OXIDE ON DIGESTION OF NICOTINIC ACID

HgO, *mg*	%N
1	8·3
5	10·75
10	11·3
20	11·3
40	11·3
100	11·2

independently, but that either or both will be influenced by the nature of the sample and the conditions of digestion. The categorical (and conflicting) statements made by different workers should therefore only be applied to the particular conditions used.

It is well-known that many pyridine derivatives (*e.g.* nicotinic acid, used in the present work) are difficult to break down under Kjeldahl conditions. Furthermore, they may not char, so that there may be no visual indication of the progress of digestion. It follows, therefore, that any compound which contains a stable heterocyclic ring, or which can give one during digestion, will not only be difficult to decompose, but may give a clear digest before conversion of nitrogen to ammonia is complete.

Sorenson and Anderson,[37] as early as 1905, realised the importance of the possibility of ring formation during digestion, but their paper appears to have been virtually overlooked by subsequent workers. They concluded that it was difficult to obtain quantitative results for lysine because it could ring-close to give a piperidine carboxylic acid. This would presumably occur through a series of reactions, the overall effect of which would be:



They demonstrated that pyridine, piperidine, and substances such as lysine and lysuric acid, which could give such a ring during digestion were difficult to decompose, whereas pyrrolidine carboxylic acid, and substances such as α-amino-δ-hydroxyvaleric acid and αδ-diamino-adipic acid, which could give a five-membered ring, were relatively easy to decompose. On the other hand, if the ring-closure could lead to a piperidone rather than a piperdine, decomposition was easy. Examples of this class were piperidone itself and substituted aminopropyl malonates.

In the light of these findings, much of the apparent contradiction and confusion in the literature becomes explicable. It is apparent that those workers who have found it necessary to use long digestion times, or who have found that a lengthy "afterboil" is necessary to ensure complete digestion, have used such mild conditions that the stable six-membered rings are only very slowly attacked. The extreme case is provided by Marzadro,[38] from whose work it appears that under very mild conditions (only 0·035 g of potassium sulphate/ml, and 30 min digestion) many pyridine rings are completely unattacked. Jonnard,[39] and Chibnall, Rees and Williams,[40] also using mild conditions, found it necessary to digest for 16 and 8 hr respectively. Jonnard, in fact, concluded that even with this lengthy digestion, it was not possible to decompose proteins completely unless a "pre-reductive" treatment was given. By his normal procedure, he obtained only 86–97% recovery from tryptophane, in agreement with Van Slyke, Hiller and Dillon,[41] who could only get about 90% recovery from tryptophane or lysine, although they tried "practically all the oxidising and catalytic agents recommended in the literature".

Dunn and Rockland[42] state, rather oddly, that "lysine may be determined quantitatively with the selenium-copper catalyst only after 50 hr digestion, whereas only 26 hr were required in the absence of selenium".

On the other hand, there are more recent workers, such as Perrin,[36] and McKenzie and Wallace,[5] who have achieved complete recovery with a much shorter digestion time (15 and 20 min respectively). They have obviously used conditions sufficiently drastic to decompose pyridine rings rapidly. Both these workers reported satisfactory results for nicotinic acid and tryptophane, and, in addition, lysine was analysed without difficulty by McKenzie and Wallace, who state that the "digestion periods used by Chibnall, Rees and Williams, and the preliminary treatment considered necessary by Jonnard, are thus an indication of failure to choose optimum conditions".

It is apparent from the above discussion that the clearing time is not a valid criterion of the rate of digestion, and observations made during the present work support this. It was, for example, observed that under some conditions complete recovery of nitrogen from benzylisothiouronium chloride could be obtained even before the mixture cleared.

As the work proceeded, it appeared that the clearing time might be dependent on the intensity of heating, as well as on the other factors studied, and an experiment was carried out to check this. Six identical mixtures were prepared, each containing 1·5 ml of sulphuric acid, 1·5 g of potassium sulphate, 40 mg of mercury^{II} oxide, and 5 mg of benzylisothiouronium chloride. These were digested as usual, and the clearing times noted.

Perrin[36] has described a "boil test" for checking the intensity of heating, and it was of interest to compare the results obtained in the above experiment with such a test. Accordingly, the time taken to boil 5 ml of water in a 30-ml Kjeldahl flask was determined for each burner. The results of both these tests are shown in Table X.

TABLE X—RESULTS OF CLEARING TIME TEST AND BOIL TEST

Burner	1	2	3	4	5	6
Clearing time, *min*	10	6·5	7	5	6·5	7·5
Boil time, *sec*	60–70	50	50–55	45–50	50	50

It is seen that the two tests show a reasonable agreement, with the exception of Burner No. 6, whose characteristics may have changed (the two tests were carried out at different times). The tests confirmed our suspicion that Burner No. 1 was less efficient than the others, and it was, for that reason, used throughout for the "blank" determination.

It is suggested that similar tests should be carried out by future authors to enable valid comparisons to be made.

When the clearing times for benzylisothiouronium chloride with varying concentrations of potassium sulphate were tabulated, it appeared that those digests containing over 2·0 g/ml were clearing more slowly than those with 1·0 g/ml. To check this unexpected finding, a series of otherwise identical mixtures (1·5 ml of sulphuric acid, 40 mg of mercury^{II} oxide, and 5 mg of benzylisothiouronium chloride) containing different amounts of potassium sulphate, were prepared and heated. The observed clearing times are shown in Table XI.

These results amply demonstrated that there was an optimum concentration of potassium sulphate for rapid clearing. Stubblefield and De Turk[24] attributed variations

TABLE XI—CLEARING TIMES WITH DIFFERENT AMOUNTS OF POTASSIUM SULPHATE

K_2SO_4, *g/ml*	0	0·5	1·0	1·5	2·0	2·5
Clearing time, *min*	16	9	5·5	9·5	11	17

in the digestion time to variations in the number of bubbles formed during boiling, and it is possible that a similar effect occurred here. Since the gas burner settings were the same for all digestions, the more concentrated solutions, having higher boiling points, boiled less vigorously than the others, and this factor may have overridden the effect of rise in boiling point. Another possible reason is that the digests containing more than 1·0 g of salt/ml frothed badly during the early stages of the digestion, and it appeared that much of the carbon was held in the relatively cool foam, almost unattacked by the boiling acid beneath.

The question then arose whether the frothing was characteristic of the sample used, or whether it was inherent at high concentrations of sulphate. Similar experiments were therefore carried out with a number of other organic compounds. In every case a minimum clearing time was observed at 1·0 — 1·5 g of potassium sulphate/ml, and in some cases the most concentrated digest tended to froth, but in no case was the frothing as severe as with benzylisothiouronium chloride.

RECOMMENDED METHOD

(The reagents are described on p. 61)

Weigh about 5 mg of the sample into a Kjeldahl flask. Add 20 mg of mercury^{II} oxide, 2·25 g of potassium sulphate, and 1·5 ml of sulphuric acid. Heat gently for 2–3 min to dissolve most of the salt, then at full heat for 20 min. The heaters should be checked with a "clearing time" test or a "boil test", as described on p. 68. The recommended times are 6 ± 1 min or 50 ± 5 sec, respectively.

Allow the flask to cool; dilute the contents with about 10 ml of water, and warm gently if necessary, to dissolve the "cake" of potassium hydrogen sulphate.

Wash the contents of the flask into a distillation apparatus, and add 10 ml of alkaline thiosulphate. Steam-distil the ammonia into 5 ml of boric acid, containing 4 drops of screened indicator. Allow distillation to proceed, at 4–5 ml/min, for 3 min with the tip of the condenser immersed in the boric acid, and a further 1 min with the tip clear of the surface. Wash down the end of the condenser, and titrate the contents of the receiver against 0·01*N* hydrochloric acid. Carry out a similar blank determination, and correct the result accordingly.

Some results obtained by this method are shown in Table XII.

CONCLUSIONS

The boiling points of solutions of up to 3·0 g of potassium sulphate in 1·5 g of sulphuric acid (2·0 g/ml) have been determined. In actual digestions, it has been found that in the absence of any catalyst, no loss of nitrogen occurs with a salt concentration of up to 2·5 g/ml (corresponding with an estimated temperature of 430°). Because of frothing and extended clearing times, however, the maximum practical concentration is 1·5 g/ml.

Mercury, used alone, is the best catalyst, under the conditions investigated. All other catalysts examined either cause a loss of nitrogen, or are inferior to mercury with regard to the rate of digestion.

Using mercury as catalyst, together with a salt concentration of 1·5 g/ml, quantitative results have been obtained on all of the compounds examined, with a digestion time of only 20 min.

TABLE XII—RESULTS OBTAINED BY THE RECOMMENDED METHOD

Compound	% Nitrogen	
	Required	Found
Nicotinamide	22·9	22·7
Histidine hydrochloride monohydrate	20·15	19·75
Lysine monohydrochloride	15·35	15·1
Tryptophane	13·7	13·6
Atropine	4·85	4·75
4-Hydroxy-1,2,2,6,6-pentamethylpiperidine oxalate	5·35	5·4
α-Naphthoxyacetonitrile	7·65	7·7
2-Oximino-3-phenoxybutane	7·8	7·8
8-ω-Bromovaleramido-6-ethoxyquinoline	8·0	7·8
N,*N*-Diamyl-*N*′-phenylguanidine	15·3	15·3
1,2,3,4-Tetrahydro-β-carboline	16·25	16·0
Cyclopentylguanidine sulphate	23·85	23·8
Trimethylenethiourea	24·15	24·2

The clearing time has been shown to be of no value as a measure of the rate of digestion. The intensity of heating may significantly affect the rate of digestion, and it is suggested that future authors should carry out a "boil test", or a "clearing time" test, to enable their conditions to be duplicated by other workers.

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Zusammenfassung—Die Einwirkung des Titers der Kaliumsulfatlösung—und 21 einzelner und gemischter Katalysatoren—auf die Bestimmung des Stickstoffes mittels der Kjeldahl-Methode wurde untersucht. Quecksilber hat sich als der beste Katalysator erwiesen. Ein höherer Titer der Kaliumsulfatlösung als der sonst übliche wird empfohlen. Es werden verschiedene Faktoren besprochen, u.a. auch die "Entfarbungszeit" ("clearing time"), die sich auf die Bestimmung auswirken.

Résumé—Les effets du titre de la solution en sulfate de potasse et de 21 catalyseurs simples et mixtes sur la détermination de l'azote par la méthode de Kjeldahl, ont été étudiés. Le mercure s'est confirmé comme le meilleur catalyseur et un titre en sulfate de potasse plus élevé que le titre habituel est recommandé. La communication contient des commentaires au sujet de divers facteurs, y compris le "temps de décoloration" ("clearing time"), qui entrent en jeu dans la détermination.

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THE CO-CRYSTALLISATION OF ULTRAMICRO QUANTITIES OF MOLYBDENUM WITH α-BENZOINOXIME

DETERMINATION OF MOLYBDENUM IN SEA WATER

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Summary—The co-crystallisation of ultramicro quantities of molybdenum with α-benzoinoxime was studied and conditions were established for the quantitative recovery of this element from very dilute solution. The information derived from these experiments was applied to the isolation and determination of molybdenum in sea water. After radiometric correction for its yield, the concentration of molybdenum in sea water was determined to be 12·2 ± 0·1 μg/litre.

INTRODUCTION

ELEMENTS are often collected and concentrated from very dilute solution by co-precipitation with an inorganic carrier. In the case of trace amounts of molybdenum, separation is generally accomplished by co-precipitation with an iron carrier. Although this procedure is effective, insoluble iron salts also efficiently scavenge many other elements; thereby the ultimate purification process may be more difficult as compared with a method which is more discriminating.

Organic reagents as a rule are more selective as carriers, and greater specificity in fact was achieved by co-precipitating molybdenum from natural waters with tannin and methyl violet.[1] Furthermore, by virtue of the ability to remove the organic reagent by simple procedures, such processes are in essence carrier-free.

As a continuation of a general study on the separation of ultramicro quantities of elements from solution by co-crystallisation with organic precipitants, the collection of trace amounts of molybdenum with α-benzoinoxime was studied. This reagent was selected because its molybdenum salt satisfies Fajans Rule.[2] The value of this rule in the choice of an organic compound was previously established.[3]

The co-crystallisation of molybdenum upon crystallisation of fractions of the carrier from solution, the influence of oxime concentration, and the effect of pH were studied. To provide for the accurate measurement of ultramicro quantities of molybdenum, a radioactive tracer was used. The information derived from these experiments was applied to the isolation and determination of the natural molybdenum content of sea water.

EXPERIMENTAL

Reagents

α-Benzoinoxime (Eastman Kodak): Purified by recrystallisation from alcohol. The purified reagent was dissolved in acetone several hr before use.

Buffer solution (pH 5·5): Prepared from analytical reagent-grade acetic acid and sodium acetate. Other chemicals used were of analytical reagent-grade.

Molybdenum-99 tracer: isolated carrier-free from a fresh uranium fission-product mixture.[4] The final solution was 0·1N in nitric acid and molybdenum was in the sexavalent state. Radiochemical purity was established by γ photon pulse height analysis and by decay measurements. The γ photon measurements were made in a well scintillation counter.

Spectrophotometric determination of α-benzoinoxime

To evaluate upon crystallisation the distribution of α-benzoinoxime between the liquid and solid phase, a spectrophotometric method was developed for its determination. With a Beckman spectrophotometer the maximum spectral absorption occurred at 251 mμ when α-benzoinoxime was dissolved in the buffer solution. The optical density at this wavelength of 5 to 20 μg of oxime per ml of solution when compared to a solution blank is shown in Table I. The relation between reagent concentration and optical density adhered to Beer's Law.

TABLE I.—THE OPTICAL DENSITY AT 251 mμ OF DIFFERENT CONCENTRATIONS OF α-BENZOINOXIME IN ACETATE BUFFER (pH 5·5)

α-Benzoinoxime, *μg/ml*	Optical density
5	0·251
10	0·495
15	0·745
20	0·985

The α-benzoinoxime distribution was determined by assay of the crystalline phase. After crystallisation, the crystals were collected on paper by filtration through a tower, then dried for several min with the aid of suction. The collected material was dissolved in absolute ethyl alcohol and diluted to a definite volume. An aliquot of this solution was diluted to the spectral working range with acetate buffer and its optical density was compared with a blank buffer solution which contained a like concentration of ethyl alcohol. The concentration of α-benzoinoxime was computed from the optical density measurement in the usual manner.

Experimental method

One ml of carrier-free molybdenum-99 with a γ photon activity of 10^4–10^5 cpm was added to 10 ml of water whose hydrogen ion concentration was previously adjusted with sulphuric acid or sodium hydroxide. Five ml of α-benzoinoxime solution were added. The resultant homogeneous solution was heated in a steam bath until part or nearly all of the acetone was evaporated. The sample was then cooled in an ice bath and the phases were separated by filtration. The molybdenum distribution was determined by γ-photon measurement of the crystal phase after solubilisation of the oxime and dilution to volume with ethyl alcohol. The measurement was made after the establishment of equilibrium between molybdenum-99 and its daughter technetium-99. This alcohol solution was analysed also for oxime.

RESULTS AND DISCUSSION

The effect of the organic reagent concentration over the range 30 to 200 mg of oxime per sample upon the co-crystallisation of molybdenum is shown in Table II. Samples were boiled until they were reduced to their original aqueous volume. At the lower reagent concentration only 15·5% of the oxime crystallised from solution and this fraction carried 25% of the molybdenum. At an oxime concentration of 120 to 200 mg per sample more than 90% of the oxime was recoverable and under these conditions molybdenum was carried quantitatively.

The effect of the hydrogen ion concentration upon the recovery of molybdenum tracer is shown in Table III. In this series the reagent concentration was 200 mg per sample. Molybdenum was quantitatively recovered over the pH range 1·8 to 5·5.

TABLE II.—THE RECOVERY OF MOLYBDENUM AND α-BENZOINOXIME FROM SOLUTIONS WHICH CONTAIN DIFFERENT QUANTITIES OF THE ORGANIC REAGENT

α-Benzoinoxime added, *mg*	α-Benzoinoxime crystallised, %	Molybdenum-99 tracer recovered, %
30	15·5	25·0
60	68·3	85·7
120	93·3	100·0
200	91·0	100·0

TABLE III.—THE EFFECT OF pH UPON THE CO-CRYSTALLISATION OF MOLYBDENUM TRACER WITH α-BENZOINOXIME

pH	Molybdenum-99 recovered, %
(1·6*N* H_2SO_4) 0	54·6
1·8	100·0
3·7	99·0
5·5	99·4
8·0	94·6
10·5	6·1

The recovery of molybdenum tracer was determined at pH 1·5 with 200 mg of reagent. In this series the degree of crystallisation was varied. When 58·8% of the oxime crystallised, 94·9% of the molybdenum was carried, whereas the micro component was recovered quantitatively when about 80% of the precipitant was crystallised (Table IV).

The results show that the crystalline phase was enriched with the micro component. The degree of enrichment was such that quantitative recovery of molybdenum tracer was assured when a suitable quantity of oxime was introduced into the solution.

TABLE IV.—THE RECOVERY OF MOLYBDENUM TRACER WITH DIFFERENT QUANTITIES OF CRYSTALLISED α-BENZOINOXIME

α-Benzoinoxime crystallised, %	Molybdenum-99 recovered, %
58·5	94·9
75·0	98·4
78·3	98·8
82·5	100·1
87·6	100·0
91·0	100·0
93·1	99·3
93·7	100·0

Furthermore, the optimum pH range was the same as that at which the macro precipitation reactions occur most effectively. These facts again indicate that in the co-crystallisation process the micro component combines with the organic reagent and is internally incorporated in the crystal lattice rather than surface adsorbed.[3]

Determination of the molybdenum content of sea-water

The molybdenum content of sea water has been previously reported as 0·5,[5] 3[6] and 11[7] μg/litre. The quantitative methods used were predicated upon the preliminary concentration of molybdenum from the medium by co-precipitation with an iron carrier.

The method to be described was based upon the concentration of molybdenum from sea water by co-crystallisation with α-benzoinoxime. Following this separation the oxime was eliminated by acid oxidation, molybdenum was purified by ion-exchange, and quantitatively determined colorimetrically. Radiometric correction for losses of molybdenum incurred during the analytical procedures was applied.

Separation of molybdenum from sea water

To examine the co-crystallisation of molybdenum from sea water, 1 ml of tracer was added to 10 ml of sea water previously adjusted to pH 2 with sulphuric acid. One drop of bromine was added to each of two of the four samples in the series Five ml of acetone containing 120 mg of the oxime were added, the carrier was crystallised by reducing the volume to 11 ml and the molybdenum recovery was determined. The results appear in Table V. Molybdenum was recovered quantitatively when oxidised to the sexavalent state with bromine. In the non-brominated acidified sea water samples the microcomponent was apparently partially reduced (molybdenum is sexavalent in untreated sea water[8]) and therefore incompletely recovered.

TABLE V.—CO-CRYSTALLISATION OF MOLYBDENUM IN SEA WATER WITH α-BENZOINOXIME

Sample	Molybdenum recovered, %	
	Bromine-treated	Untreated
1	99·1	
2	98·9	
3		94·3
4		93·8

Procedure

The analytical procedure was applied to surface sea water collected 40 miles due west of San Francisco. To sample aliquots of 2, 4, 6 and 8 litres was added carrier-free molybdenum tracer. The pH of the separate aliquots was adjusted to 2 with sulphuric acid. The solution was treated with bromine water (0·1 ml/litre of sample). α-Benzoinoxime was added (1·2 g in 32 ml of acetone/litre of sample). The solution was boiled until reduced to the original sea water volume. After standing at room temperature overnight, the crystals were collected on sintered-glass and dissolved therefrom with acetone. The acetone was evaporated, and the residue was wet-ashed with sulphuric acid and a 50:50 mixture of nitric acid-perchloric acid. The completely ashed and colourless solution was evaporated to near-dryness. After cooling, 15 ml of concentrated hydrochloric acid were added and the solution was passed through a column of Dowex 2 (10 cm long, 0·6 cm diameter) previously washed with concentrated hydrochloric acid. The column was washed with 20 ml of concentrated hydrochloric acid, and molybdenum was eluted with 20 ml of 12*N* nitric acid. The eluate was evaporated to dryness, then dissolved in 1-4 ml of 8*N* hydrochloric acid. Each sample was diluted to 25 ml with distilled water and the molybdenum yield was determined radiometrically at this stage of the analysis by comparison with the molybdenum-99 control diluted to the same volume. The molybdenum content of this solution was then determined by a thiocyanate spectrophotometric procedure.[9]

RESULTS

The results of four analyses appear in Table VI. The average molybdenum content of the sea water sample analysed was 12·2 ± 0·1 μg/litre and this value is consistent with that reported by Ishibashi.[6] The main errors in the analysis are attributable to the radioactive counting statistics and the spectrophotometric measurements, and these were approximately 0·5% and 3%, respectively. Furthermore, the fact that the molybdenum content was identical for samples of different size indicates that analytical interferences were absent and that the results, therefore, are reliable.

TABLE VI.—MOLYBDENUM CONTENT OF SEA WATER

Sea water sample volume, *litres*	Molybdenum content, *μg/litre*
2	12·3
4	12·3
6	12·0
8	12·1
	Average 12·2 ± 0·1

Zusammenfassung—Die Cokristallisation von Ultramikromengen Molybdän mit Benzoinoxim wurde studiert und die Bedingungen festgestellt um dieses Element quantitativ aus sehr verdünnten Lösungen abzutrennen. Die gewonnenen Erkenntnisse wurden verwendet um Molybdän in Seewasser zu bestimmen. Nach anbringen einer radiometrischen Korrektur wurde die Konzentration von Molybdän in Seewasser zu 12,2 ± 0,1 μg/Litre gefunden.

Résumé—La cocristallisation d'ultramicro quantités de molybdène avec l'alphabenzoineoxime a été étudiée et les conditions de récupération quantitative de cet élément à partir d'une solution très diluée ont été établies. Les données déduites de ces expériences ont été appliquées à l'isolement et au dosage du molybdène dans l'eau de mer. Après une correction radiométrique pour son rendement, on a trouvé que la concentration du molybdène dans l'eau de mer était de 12,2 ± 0,1 μg/l.

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ANALYTICAL USE OF 1,3-DIMETHYL-4-IMINO-5-OXIMINO-ALLOXAN—I

DETERMINATION OF COPPER

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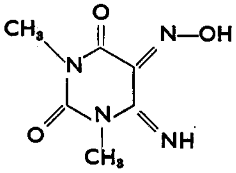
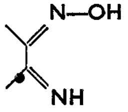
Summary—The use of a new organic reagent for metals, 1,3-dimethyl-4-imino-5-oximino-alloxan (DAXIM) is proposed. The acid dissociation constant of this compound has been established by potentiometric titration. The composition and the stability constant of its copper complex have been determined spectrophotometrically. An absorptiometric method has been evolved for the determination of micro amounts (1–13 μg/ml) of copper using DAXIM. The new method has proved suitable in the presence of large amounts of mercury^{II}, lead, bismuth, manganese and zinc, and of smaller amounts of iron^{III}, aluminium and certain other metals. The preparation of the reagent is described.

The object of the present investigation was to find, for use as reagents for metals, organic molecules containing two or more functional groups selective for certain metals, but possessing a structure enabling them to form with a number of metals (not more than three or four) coloured, water-soluble complexes, and forming precipitates with only one or two metals. Thus it would be possible to use the same reagent, under various conditions, for the selective determination of several metals.

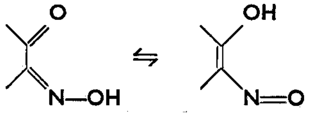
As a first result of the investigations, the use of 1,3-dimethyl-4-imino-5-oximino-alloxan (abbreviated as DAXIM) as an organic microanalytical reagent is suggested:



This molecule contains two characteristic functional groups: an isonitroso-imino group (1), selective for nickel and palladium^{II}, and an isonitroso-keto and nitroso-enol equilibrium (2), selective for iron^{II}, copper^{II} and cobalt^{II}:



(1)



(2)

DAXIM can be prepared simply by Traube synthesis, can be purified by recrystallisation from hot water, and is an inexpensive reagent, readily available as an intermediate in the production of theophylline.

DAXIM is a crimson crystalline substance, practically insoluble in most of the conventional solvents (chloroform, alcohols, ether, dioxan, *etc.*), very poorly soluble in acetone and in water, but readily soluble in formamide. In the present experiments, a 1–10% solution in formamide was used. DAXIM dissolves in alkalis with the formation of a brownish-red salt.

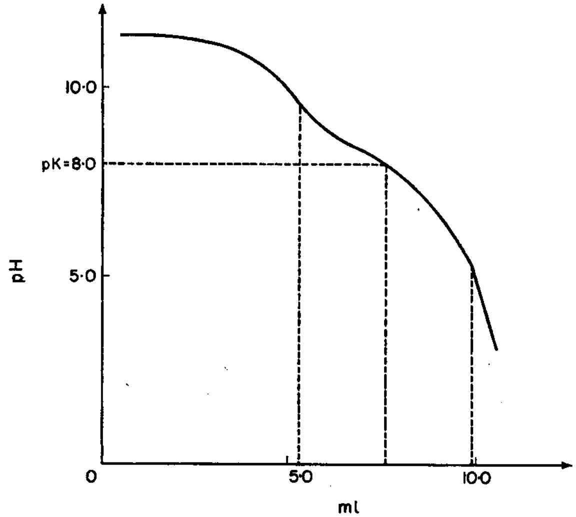


FIG. 1.—Potentiometric titration of a mixture of 0·0846 g of DAXIM and 5·00 ml of 0·2*M* sodium hydroxide with 0·1*N* hydrochloric acid using glass and saturated calomel electrodes.

Potentiometric titration of the alkaline solution of DAXIM (Fig. 1) gave an acidic dissociation exponent, p$K = 8$.

The absorption curve (Fig. 2, curve 1) of the aqueous solution of DAXIM ($2 . 10^{-2}$

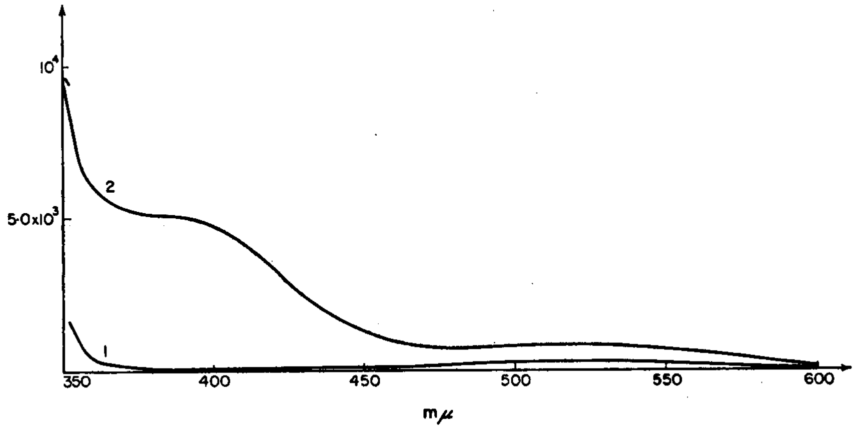


FIG. 2.—(1) Absorption spectrum of DAXIM.
(2) Absorption spectrum of the copper complex of DAXIM.

molar), containing about 4–5% of formamide, showed a maximum at 530 mμ, and no absorption was observed from 370 to 460 mμ and above 600 mμ.

As might be expected on the basis of its structure, DAXIM forms a water-soluble coloured complex with copper^{II}, iron^{II}, and cobalt^{II} ions, and a practically insoluble precipitate when boiled with palladium in a slightly acidic medium, or with nickel in ammonia.

In neutral or slightly alkaline aqueous solution, copper^{II} ions form with DAXIM a water-soluble complex, insoluble in non-polar solvents. The complex is grass-green, and shows a red tint with excess of the reagent. Its absorption curve (Fig. 2, curve 2) is uniform in the range 380–390 mμ. In this region no light is absorbed by the reagent itself, and therefore in further experiments the extinction values were measured at a wavelength of 382 mμ.

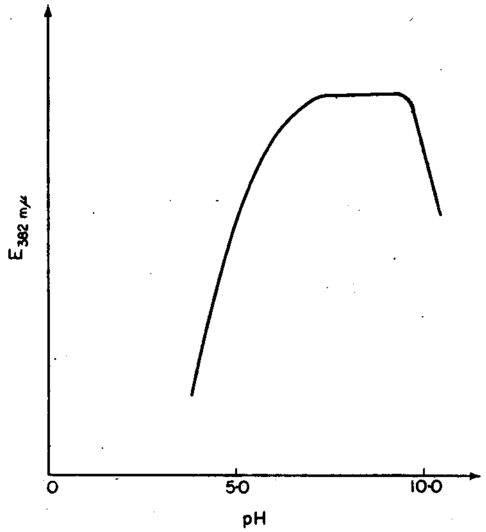
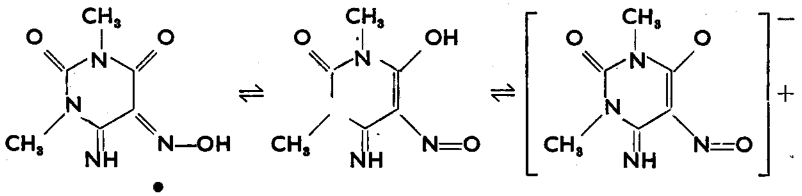


FIG. 3.—Correlation of the copper complex of DAXIM with pH values.

The dependence of extinction values upon pH values was established at a copper^{II} concentration of 2 . 10^{-4} moles/litre and a reagent concentration of 8 . 10^{-4} moles/litre. As appears from Fig. 3, the maximum extinction with this concentration of the complex is between pH 7 and pH 9·5. On considering the acidic dissociation exponent of DAXIM, pK = 8, the dissociated molecules of the reagent must take place in the complex formation. Presumably a keto-enol conversion precedes the dissociation:



In order to establish the stoichiometric composition of the complex, a Job's curve[1] was plotted in a Britton-Robinson buffer of pH 8 (Fig. 4). This indicates that copper^{II}

ions form a 1 : 1 complex with DAXIM. Therefore only two of the four co-ordination points of copper may participate in the chelate formation, both residual co-ordination points being occupied by water molecules, or monofunctionally by DAXIM in the case of a great excess of reagent. This is why raising the excess of reagent increases the value of the extinction coefficient.

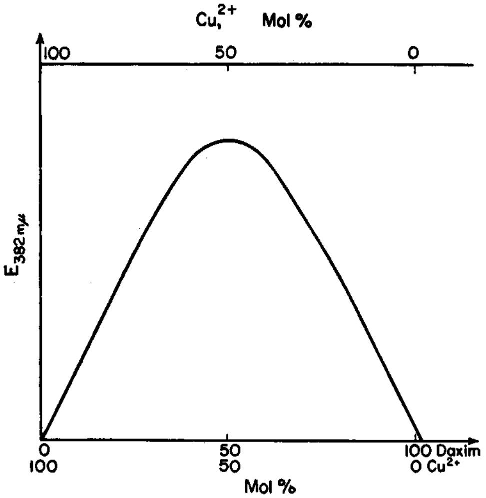
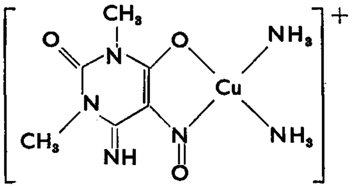


Fig. 4.—Job's curve of continuous variation. At a 1:1 ratio, the concentration of the complex was 2 × 10^{-4} mole/litre.

Further experiments carried out in a buffer containing ammonia suggest that in the complex formed under these conditions, two co-ordination points of copper are occupied by a DAXIM molecule and the other two by ammonia molecules:



Electrophoretic measurements also supported the above structure of the complex.

It was apparent from Job's curve, that the extinction of the complex obeys the Lambert-Beer law in the case of a large excess of reagent (over 80 mole %), and that the value of the extinction coefficient is not affected by any further increase in the excess of reagent. In further experiments the amount of reagent used was four to twenty times the theoretical value. In order to establish the molar extinction coefficient, the extinction values of various complexes prepared in copper^{II} solutions of various known concentrations (Fig. 5) were measured. It was found that in solutions containing 1–13 μg/ml of copper^{II} ions the molar extinction coefficient was

$$\varepsilon = (5{\cdot}05 \pm 0{\cdot}05) \times 10^3 \text{ (mean value of 24 measurements)}$$
$$\text{at } 25^\circ \text{ and a wavelength of } 382\ \text{m}\mu.$$

From the knowledge of the extinction coefficient, the stability constant of the complex was calculated using the value for the extinction measured at the maximum of the Job's curve (*i.e.* from the extinction value of the complex of stoichiometric composition). At a given pH (pH = 8) the concentration of the ligand formed by

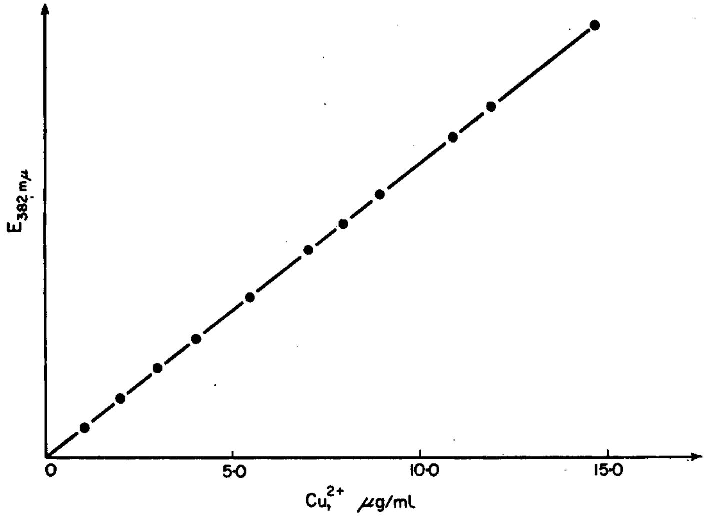


FIG. 5.—Correlation with concentration in a Britton-Robinson buffer solution of pH 8, containing 0·1% of ammonium chloride; volume, 25 ml.

dissociation of the complex was calculated from the acidic dissociation exponent of DAXIM (pK = 8) and from the dissociation exponent of ammonium hydroxide (pK = 4·74).

The stability constant of the complex is:

$$K = \frac{[\mathrm{Cu{\cdot}DAXIM{\cdot}(NH_3)_2{}^+}]}{[\mathrm{Cu^{2+}}]{\cdot}[\mathrm{DAXIM}]{\cdot}[\mathrm{NH^3}]^2} = \frac{1{\cdot}6 \times 10^{-4}}{1{\cdot}58 \times 10^{-24}} = 10^{20}$$

$$pK = 20$$

On the basis of the molar extinction coefficients and of the calculated factor, it was possible to use DAXIM for the photometric determination of micro amounts (1–13 μg/ml) of copper$^{\mathrm{II}}$. Results are summarised in Table I and Fig. 5. It can be seen from Table I that the error of the method is ±2% even if the copper concentration is 1–2 μg of Cu/ml.

In order to establish how far certain metals might interfere in this determination, experiments were carried out at pH = 8 in a Britton-Robinson buffer-solution containing 0·1% of ammonium chloride and in certain cases in a buffer solution of ammonia and ammonium chloride of pH 8. The solution of unknown copper content was first treated with the reagent dissolved in formamide, and buffer solution was then added in the amount necessary to obtain a solution containing 1–13 μg of Cu/ml. In the case of metal ions which form precipitates with the buffer solution, the turbid solution was centrifuged, and the supernatant liquid was decanted (not filtered). The precipitate was stirred with a few millilitres of water and centrifuged, and the former solution was diluted with this water to known volume. Before measuring extinction values, if necessary, the solution was adjusted by further portions of buffer solution to a pH value of 7–9.

The analytical results obtained from some experiments are presented in Table II. As can be seen, it was possible to determine about 7 μg/ml of copper with an error of ±2–3%, in the presence of 500 times this amount of mercury^{II}, of 100 times this amount of lead, and of appreciable quantities of manganese, bismuth, zinc, cadmium, iron^{III} and other metals.

TABLE I.—DETERMINATION OF COPPER

Copper weighed, *μg/ml*	Extinction (382 mμ)	Copper found, *μg/ml*	Δ, *μg/ml*	Δ,%
0·96	0·076	0·958	−0·002	−0·2
	0·077	0·970	+0·01	+1·0
1·92	0·149	1·88	−0·04	−2·1
	0·151	1·90	−0·02	−1·5
3·00	0·238	3·00	0·00	0·0
	0·236	2·97	−0·03	−1·0
3·83	0·304	3·83	0·00	0·0
	0·307	3·87	+0·04	+1·0
5·00	0·397	5·00	0·00	0·0
	0·396	4·99	−0·01	−0·2
6·13	0·488	6·15	+0·02	+0·3
	0·480	6·05	−0·08	−1·3
7·66	0·608	7·66	0·00	0·0
	0·600	7·56	−0·10	−1·3
10·0	0·790	9·95	−0·05	−0·5
	0·788	9·93	−0·07	−0·7
12·04	0·953	12·00	−0·04	−0·3
	0·960	12·10	+0·06	+0·5
	1·010	12·72	−0·05	−0·4
12·77	0·995	12·54	−0·23	−1·8
	0·990	12·47	−0·30	−2·3

TABLE 2.—INTERFERENCES

Copper weighed, *μg/ml*	Metal ion present	Amount of metal ion present, *μg/ml*	Extinction (382 mμ)	Copper found, *μg*/ml	Δ, *μg/ml*	Δ,%
7·66	Hg^{2+}	4000	0·592	7·46	−0·20	−2·6
	Hg^{2+}	1600	0·596	7·51	−0·15	−2·0
	Pb^{2+}	830	0·620	7·81	+0·15	+2·0
	Bi^{3+}	250	0·610	7·69	+0·03	+0·4
	Mn^{2+}	220	0·608	7·66	0·00	0·0
	Zn^{2+}	260	0·600	7·56	−0·10	−1·3
	Cd^{2+}	440	0·589	7·42	−0·24	−3·1
	Ba^{2+}	560	0·600	7·56	−0·10	−1·3
	Fe^{3+}	68	0·620	7·81	+0·15	+2·0
	Al^{3+}	32	0·600	7·56	−0·10	−1·3
	Ca^{2+}	160	0·620	7·81	+0·15	+2·0
	Mg^{2+}	96	0·610	7·69	+0·03	+0·4
	Na^{+}	100	0·608	7·66	0·00	0·0
	Sb^{3+}	500	0·595	7·49	−0·17	−2·2

Consideration of the various methods already proposed for the determination of copper in the same concentration region shows, that of the metals listed in Table II, mercury^{II} and bismuth interfere in the dithizone method;[2] iron^{III}, bismuth and manganese in the diethyldithiocarbamate method;[3] manganese, magnesium, lead and mercury^{II} in the *m*-benzaminosemicarbazide method;[4] zinc and mercury^{II} in the urobiline method;[5] and lead and antimony in the rubeanic acid method[6].

The present investigations showed that small amounts of cobalt, palladium, nickel and iron^{II} interfere in the determination of copper by DAXIM. Thus, before using this reagent, copper must be separated from these metals and iron^{II} must be oxidised to iron^{III} with hydrogen peroxide.

Further experiments on the use of DAXIM for the selective micro-determination of other metals (palladium, iron^{II} and cobalt) are in progress.

EXPERIMENTAL

Preparation of 1,3-*dimethyl-4-imino-5-oximino-alloxan*

Reagents required

Ethanol, anhydrous.
Sodium metal.
Ethyl cyano-acetate.
Urea.
Dimethyl sulphate.
Sodium hydroxide, 40%.
Sodium nitrite.
Acetic acid, glacial.
Acetic acid, 50%.

Preparation

Cautiously dissolve 9·6 g of small pieces of metallic sodium in 240 ml of anhydrous ethanol, then add dropwise 22·6 g of freshly distilled ethyl cyano-acetate with continuous stirring. Add 12 g of previously dried urea to the mixture, when a white precipitate which is formed will dissolve. Keep the reaction mixture boiling for 3 hr on the water bath under a reflux condenser, filter the white precipitate after cooling, dry it by suction, and dissolve it in 60–80 ml of water. Adjust the pH of this solution to 5–6 with 50% acetic acid, using universal indicator paper. Filter the precipitate of 2,6-*dioxo-4-imino-hexahydropyrimidine,* wash it with 2 × 10 ml of cold water and dry it at room temperature.

Treat the aqueous suspension of 12·7 g of this product dropwise under continuous stirring, with 23·8 ml of dimethyl sulphate and 25 ml of 40% sodium hydroxide. The pH of the reaction mixture must be between 8 and 9. If the liquid becomes hot, apply cooling. Stir for 2 hr, filter the precipitate of 1,3-*dimethyl-2,6-dioxy-4-imino-hexahydropyrimidine,* wash it with 3 × 20 ml of water and dry it at room temperature.

Dissolve 11·6 g of the product in 300 ml of boiling water, filter the hot solution, add 6·2 g of sodium nitrite, allow the mixture to stand for 0·5 hr, and acidify the solution with 5·6 ml of glacial acetic acid. The liquid slowly turns dark bordeaux, and 1,3-*dimethyl-4-imino-5-oximino-alloxan* (DAXIM) precipitates as crimson coloured crystals. In order to complete the crystallisation, cool the reaction mixture in melting ice, transfer the product to a filter, and dry it at 100°.

For analytical procedures the substance was repeatedly recrystallised from hot water.

Analytical method

Reagents

DAXIM in formamide: 0·05*M* (about 1%) solution.
Britton-Robinson buffer solution of pH 8, containing 0·1% of ammonium chloride.
Hydrochloric acid, 2*N*.
Sodium hydroxide, 2*N*.

Procedure:

Evaporate aliquots of the solution containing 10–130 μg of copper to 1–2 ml, neutralise approximately with 2*N* alkali or acid in the presence of universal indicator paper, and if necessary reduce again to small volume, then treat with 0·4 ml of a 1% solution of DAXIM, and with 5–6 ml of the buffer solution. If the solution contains ions forming a precipitate with the buffer solution, it is advisable to mix the reagents in a centrifuge tube, and to separate the precipitate from the supernatant liquid. On decanting the liquid, mix the precipitate with 1–2 ml of water, and again centrifuge. Measure the pH value of the combined solutions with universal indicator paper. Dilute the solution, of pH 7–9, to 10·00 ml, and measure the extinction value at 382 mμ in a 1-cm cuvette.

Multiply the extinction value by 12·6 to obtain the copper content (in micrograms) of 1 ml of solution.

In the case of higher copper concentrations, the volume of liquid can be greater (*i.e.* 25, 50 or 100 ml instead of 10 ml). Obviously, appropriately greater amounts of reagent and buffer solution should then be used.

In the present experiments, a solution prepared from exactly weighed portions of crystalline copper^{II} sulphate ($CuSO_4 \cdot 5H_2O$) of analytical grade was used, and was controlled by iodimetry and electrogravimetry.

For measuring the absorption spectra and for carrying out the photometric measurements, a Beckman DU quartz spectrophotometer and 1-cm quartz cuvettes were used, a tungsten filament serving as light source.

Acknowledgement—Thanks are due to Mr. L. Ladányi for carrying out the organic preparative procedures.

Zusammenfassung—1,3-Dimethylalloxan-4-imid-5-oxim (DAXIM) wird als neues Reagens für Metallionen vorgeschlagen. Die saure Dissoziations-konstante der Substanz wurde durch potentiometrische Titration ermittelt. Die Zusammensetzung des Kupferkomplexes der Substanz wurde photometrische bestimmt und die Stabilitätskonstante berechnet. Eine photometrische Mikromethode (1–13 μg per ml) zur Bestimmung von Kupfer wurde entwickelt. Die Methode arbeitet korrekt in Gegenwart grosser Mengen von Quecksilber (II), Wismuth, Blei, Mangan und Zink sowie kleineren Mengen von Eisen (III), Aluminium und einer Anzahl anderer Metalle. Die Synthese des Reagenzes ist beschrieben.

Résumé—L'auteur propose l'utilisation d'un nouveau réactif organique pour les métaux, la 1,3-diméthylalloxane-4-imide-5-oxime (DAXIM). La constante d'acidité de ce composé a été établie par titrage potentiométrique. La composition de son complexe avec le cuivre a été déterminée par photométrie et sa stabilité a été mesurée. L'auteur quantités (1–13 μg par ml) de cuivre, utilisant la DAXIM. La méthode convient en présence de grandes quantités de mercure (II), plomb, bismuth, manganese et zinc et de plus faibles quantités de fer (III), aluminium et d'un certain nombre d'autres métaux. La préparation du réactif est décrite.

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A CRITICAL EXAMINATION OF THE GRAVIMETRIC AND TITRIMETRIC METHODS FOR THE DETERMINATION OF GOLD

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Summary—This survey covers pertinent literature published before July 1960. An attempt has been made to identify the most generally applicable titrimetric and gravimetric methods for determining gold. While certain methods have been rejected from this point of view, it is admitted that, where many determinations are involved and the qualitative compositions are approximately constant, some of these methods may be particularly effective. Because of its wide application, the precipitation of gold from cyanide solutions is treated separately. The controversial character of the iodometric method for gold has been emphasised.

THE origins of methods for extracting gold from natural sources reach far into antiquity. From the very advent of scientific literature extractive procedures have been recorded, until at the present time the separation and determination of gold is a subject of discussion in practically all issues of chemical abstracts. Because of the wide applications of this metal, extending as they do into the fields of medicine, decorative alloys, monetary systems *etc.*, extractive methods are of many types, among which solvent extraction processes predominate. A rather wide choice of these is available and they include treatment of both fused and aqueous systems.

Initially it was hoped to discuss in a single review the recorded methods of isolation and determination but the large accumulation of pertinent literature made this inadvisable. The present review will be confined to the classical methods of determination; and subsequent discussions will deal with the "instrumental methods" and the procedures for isolating gold from both solid and liquid systems. More than one hundred published procedures deal specifically with the gravimetric determination of gold, and at least as many more are concerned with this determination as an integral part of a more general analytical scheme. This situation is not surprising, since a large number of available methods for a metal constituent is practically always associated with the ease of discovery of new reagents for that constituent: and few metals respond to a greater variety of precipitants. Generally this characteristic is found with predominately bivalent or quadrivalent metals; but in the case of gold, with a reduction potential of −1·4 V, the quantitative precipitation of the metal is accomplished with ease.

GRAVIMETRIC METHODS

Quantitative reduction to metal

In general, the quantitative recovery of metallic gold requires exacting techniques. To avoid loss of the fine but heavy particles of gold, one must recognise the effects of acidity, rate of addition of precipitant, period of digestion and particularly the tendency for these particles to adhere tenaciously to beaker walls. The techniques used by the present author include the initial addition of the precipitant by means of a fine capillary and the final transference of gold in the light of a flashlight placed upright beneath the beaker, assisted further by a small piece of ashless paper moved about by a stirring rod drawn to a fine stem which terminates in a small glass globule. Alternatively one may use a filtering feather sealed directly into a glass rod. As one would expect from the pertinent reduction potentials, the tendency toward the formation of fine particles will vary with the reagents used.

The optimum heating range for precipitated gold has been the subject of various investigations. Ishii[1] recommended temperatures above 230°. Kiba and Ikeda[2] used 700°. Champ, Fauconnier and Duval[3] recorded useful data which provide some explanation for the variety of optimum ignition temperatures. As one would expect, occluded organic reductant will have some influence, but a hitherto unknown phenomenon was observed in that "gold retains an amount of oxygen by adsorption, which varies according to the degree of subdivision, the nature of the precipitating reagent, and the environmental atmosphere during heating. When this phenomenon takes place the gain in weight is about 1%. It is reversible, and if the cooling curve is identical with the heating curve, exactly the same amount of oxygen is released as was taken up on heating". This characteristic is made clearly evident by heating gold precipitated by pyrogallol.

Among the many available reductants the following are more generally used: oxalic acid, sulphur dioxide, ferrous sulphate, nitrous acid, hydroquinone, dimethylglyoxime, stannous chloride, hydrogen peroxide and formic acid. Of these the first three have been most frequently applied.

In 1841 Kemp[4] used oxalic acid to separate gold from platinum, and over a century later Magdalena[5] recorded detailed directions for this precipitation. Malowan[6] recommended the addition of morpholine oxalate to the oxalic acid solution to produce an easily handled precipitate. With oxalic acid there is the advantage that excess reagent presents no problem, and the reagent is stable and readily obtained in a pure state. On the other hand a successful precipitation is peculiarly dependent upon the prior history of the gold solution. Samples which have been treated with *aqua regia*, and subsequently with hydrochloric acid, yield exceedingly fine precipitates, sometimes with a marked tendency to adhere tenaciously to the beaker walls; and not infrequently the precipitation is incomplete. These difficulties become much less evident when oxalic acid is used to precipitate gold from solutions of its pure salts. The exact cause of this difference in behaviour is not clear. In any case this method usually requires extended digestion, and other reductants are much more suitable for general work.

Ferrous sulphate and sulphur dioxide have been widely used. The former may be objectionable when a separation from other noble metals is to be achieved, since iron may interfere in subsequent precipitations. Sulphur dioxide may also interfere with subsequent determinations, *e.g.* platinum metals, and it is usually removed from the filtrate by evaporation with hydrochloric acid.

Oxalic acid, ferrous ion and sulphur dioxide are particularly sensitive to the presence of nitric acid, which must be removed before precipitation. Unless care is exercised, the required evaporation with hydrochloric acid may result in the reduction of gold. This may be avoided by the addition of sodium chloride. When the presence of salt is to be avoided, one can accomplish a satisfactory evaporation with acid alone, by watchful care and the use of small volumes of acid. The intermittent addition of large volumes of hydrochloric is always inexcusable. The use of a few ml total of acid permits the removal of nitric oxides within a few minutes. Both ferrous ion and sulphur dioxide are used in acid media, and the resulting gold is usually free from large proportions of impurities.

In 1887 Bettel[7] and Kruss and Hoffman[8] reviewed the relative efficiency of ferrous sulphate, oxalic acid and sulphur dioxide as reductants for gold. It was concluded[8] that gold was selectively reduced by the three reagents in the presence of ruthenium, rhodium and iridium, but in the presence of platinum, oxalic acid was the preferred reagent, and in the presence of palladium, sulphur dioxide was recommended. In 1937 Beamish, Russell and Seath[9] rejected both oxalic acid and sulphur dioxide as specific reductants, the former partly because of a persistent tendency to carry palladium, and the latter because of significant adsorption of platinum. Because of the tendency for the sulphur dioxide precipitate to adsorb platinum and palladium, Swanger[10] recommended re-precipitation by oxalic acid or nitrite. Lenher *et. al.*[11] preferred ferrous sulphate and nitrous acid to sulphur dioxide for the separation of gold from tellurium. With the former reagent a 1–2 % hydrochloric acid solution and a digestion period of 24 hours were recommended. To precipitate one part of gold from one thousand million parts of solution, Pollard[12] co-precipitated gold with tellurium by sulphur dioxide from $1{\cdot}2N$ hydrochloric acid. Hecht and Lamac-Brunner[13] recorded procedures for the microgravimetric determination of gold by sulphur dioxide, ferrous sulphate, hydrogen peroxide, sodium dihydrogen phosphate, 8-quinolinol and hydrogen sulphide. While little new information was provided, the publication includes an acceptable list of procedures.

Precipitation by hydrogen peroxide is one of the least acceptable methods for the reduction to gold, since the basic medium required almost eliminates any separational value and encourages the formation of a fine precipitate. Vanino and Seemann[14] partially avoided these difficulties by digesting the basic mixture to destroy hydrogen peroxide and subsequently acidifying with hydrochloric acid. Ivkovich and Shaula[15] applied a similar procedure for the precipitation of gold by superoxide from solutions containing copper and cadmium. Rossler[16] considered the peroxide reduction in acid solution as too slow to be of practical value, and recommended the addition of lithium or potassium carbonate.

Formaldehyde was used by Vanino[17] in an alkaline medium and by Awerkieff[18] in an acid medium. Neither is recommended as reasonably selective. A similar objection applies to reduction by hydrazine salts. Christensen[19,20] and Plaksin and Koyukhova[21] thus reduced gold salts in acid solution and Stammreich[22] used an ammoniacal medium.

An interesting method of determining very small amounts of gold was described by Donau.[23] The minute amounts of gold were deposited from the boiling acid solution upon small pieces of Japanese silk, which was subsequently burned on platinum foil to form an alloy which could be weighed. Associated base metals did not interfere.

Sodium chlorite[24] and hypophosphorous acid[25] have been used as reductants for gold. The former allows separation from the platinum group, while the latter will separate gold from platinum only in the absence of palladium. For general purposes neither method is recommended.

Sodium nitrite is one of the oldest and most generally used precipitants for metallic gold. An interesting application was described by Jameson,[26] who added sticks of potassium nitrite to an aqueous solution of gold, followed by concentrated sulphuric acid. The gold precipitated within a few minutes as large nodules which could be separated by decantation. Holzer and Zaussinger[27] used sodium nitrite to precipitate gold from very dilute hydrochloric acid solutions of decorative platinum alloys. Subsequently the solution was neutralised to a phenolphthalein end-point, and the filtered gold was purified by treatment with nitric acid solution. Gilchrist[28] used sodium nitrite to precipitate gold at a pH of about 1·5 (red-orange of thymol blue). The procedure contains directions for the simultaneous precipitation of indium, copper, zinc and nickel, and the subsequent selective acid extraction of the base metals. This author emphasised the precaution of washing out the nitrite before acidification of the hydroxide precipitate, to avoid dissolution of gold. Later, Gilchrist[29] stated that the reduction of gold by sodium nitrite is complete at the end-point of chlorophenol red (pH 4·8–6·4).

Hydroquinone has proved to be an effective reductant of gold in fire assay beads.[9] As compared with the older reducing reagents, there is less interference from platinum and palladium; the latter metal may be removed directly from the filtrate, but for the subsequent determination of platinum the organic matter should be destroyed. Some eight related organic reductants proved to be suitable quantitative precipitants. Procedures have been recorded for the application of hydroquinone to the analysis of alloys of copper, nickel, zinc and gold,[9] for the separation of gold from tellurium and selenium[30] and for the analysis of mill cyanide solutions.[30]

Organic precipitants

A considerable number of organic reagents have been used for the determination of gold, some of which produced either mixed precipitates or precipitates not easily freed of excess precipitant. In these instances ignition to gold is required. Relatively few organic precipitants produce easily prepared pure substances.

Citarin,[31] urotropine,[32] 8-quinolinol, tetra-ethylammonium chloride,[33] mercaptobenzothiazole[34] and dimethylglyoxime[35,36] have been used successfully. Citarin and urotropine are used in basic media and produce metallic gold. 8-Quinolinol[37] is used in ammonium acetate medium producing a mixed precipitate requiring ignition to metal. This method is not recommended. Tetra-ethylammonium chloride was used by Maynard[33] to avoid the contamination of gold by platinum and palladium associated with sulphur dioxide precipitations. The procedure involved prior precipitation by sulphur dioxide, then re-precipitation by the tetraethylammonium chloride to produce a yellow precipitate of variable composition which required reduction by sucrose before heating. The method has little or nothing to recommend it. Kuras and co-workers[34,38] used mercaptobenzothiazole in alcohol which, subsequent to the evaporation of the alcohol, precipitated a complex which was then ignited to gold. Duval[3] found that the complex was unstable and impure. For general quantitative work the method has little to recommend it. Dimethylglyoxime was first used by Wunder and Thuringer[35] as a precipitant for palladium. These authors stated that in hot hydrochloric acid metallic gold was precipitated, but no quantitative results were provided. Under similar conditions the present author[39] has isolated an organic complex which rapidly decomposed on exposure to air producing metallic gold. The composition of the yellowish plates proved to be variable, which state of affairs could be the result of rapid decomposition or of the formation of mixed crystals. In any case continued heating of the precipitating medium produced gold quantitatively.[36]

A few reagents produce organic weighing forms with the great advantages of easy transference and purification and also of providing very favourable weight factors. The thionalide of gold was suggested as a direct weighing form by Berg and Roebling,[40] but the present author has been unable to find a recorded procedure. Unemura[41] recorded the proper heating temperature as 230°. From the general failure of this reagent to provide weighing forms in its wide applications as a precipitant for other metals, one is not encouraged to expect an easily obtained pure substance with gold, nor any useful degree of specificity.

The first organic-gold weighing form was recorded in 1946.[42,3] Thiophenol in acid solution precipitated a white compound which upon ignition yielded slightly high results.[42] Duval[3] found that "the white deposit turns yellow on prolonged exposure to light, dries immediately, and has a constant weight up to 157° which satisfies the formula C_6H_5SAu to within 0·5%". The two levels of the pyrolysis curve could be used for automatic determinations since the ignited gold gave no evidence of adsorption of oxygen. Deterrents in the use of the method are the instability and disagreeable odour of the precipitant and the objectionable odour of the ignited products. Furthermore, the method is far from specific with respect to interference from platinum metals. Both platinum and palladium are quantitatively precipitated, although the associated base metals, copper, nickel and iron do not interfere.

A promising gravimetric method for gold was proposed by Harvey and Yoe.[43] The sodium salt of *N*-(*N*-bromo-*C*-tetradecylbetainyl)-*C*-tetradecylbetaine produced two complexes; one in hydrochloric acid solution containing 22·14% gold, and a second in hydrobromic acid solution containing 18·01% gold. Both could be dried to constant weight at 85°. Precipitation from hydrochloric acid resulted in coarse flocculent particles which decreased in size as the reagent was added to such a degree that filtration and washing were objectionably difficult. With 1–3*N* hydrobromic acid these processes were not adversely affected. The precipitate of unknown constitution could be weighed directly or ignited to gold, and the recorded results indicated excellent recovery over the range of about 5–10 milligrams of gold. However, precipitations at 30° or higher were incomplete, and large excesses of reagent reduced the particle size, with excesses beyond 25% increasing the solubility of the precipitate. The reagent is far from specific, with interferences from most of the platinum metals and a variety of base metals. Unfortunately the effects of iron, copper and nickel were not discussed, although a procedure was applied satisfactorily to gold ores which involved a solvent extraction in the presence of platinum metals, and in general a co-precipitation with tellurium by tin^{II} chloride. The method will have excellent application for standardisation and similar purposes, but in spite of the favourable weight factor, the relative value of the method for complex materials is quite limited.

Mahr and Denck[44] precipitated $AuCr(NH_3)_2(SCN)_4$ from a nitric acid solution containing sodium dihydrogen arsenite and Reinecke's salt. After a short digestion period, the precipitate was washed with dilute hydrochloric acid, dried and weighed. Bagbanly[45] also used Reinecke's salt in a hydrochloric acid medium and dried at 110°. This reaction is not particularly sensitive, and although it is stated that silver, mercury and thallium interfere, there is no reference to the effect of other noble metals; furthermore, no recovery values are recorded. In the present author's opinion better methods are available.

Metal reductants and other methods

Except as applied to cyanide solutions of gold, metal reductants offer few if any advantages. In some instances, for no apparent adequate reason, the precipitated gold was amalgamated with mercury which was then selectively removed. Thus Kalishev and Serebrennikov[46] used zinc and then mercury, with the claim that gold formed a compact, easily weighed residue. Tananaev and Davitashvili[47] used a tin amalgam in sulphuric or hydrochloric acid to complete a precipitation of gold and platinum in 5–10 minutes. Austin[48] used mercury to precipitate and collect gold from a solution of ore, and selectively removed mercury by nitric acid. This wet assay of ores and that of Harvey and Yoe[43] are worthy of further examination.

To a very limited degree, fuming with high-boiling acids may be applied to precipitate gold from aqueous media. Platinum may thus be co-precipitated, although with relatively less efficiency. Protopopescue[49] dissolved a gold alloy, removed silver chloride, and fused with potassium hydrogen sulphate to precipitate gold. Caul and Schoonover[50] adapted the sulphuric acid fuming procedure to the analysis of gold in dental amalgams. The insoluble material from a nitric acid solution was fumed with sulphuric acid to isolate gold selectively. Silverman[51] used fuming with perchloric acid to separate gold from aluminium-copper alloys after dissolution in nitric-hydrochloric acids; the isolation of gold was completed by treating the perchloric solution with formic acid to separate the traces remaining in solution. One cannot recommend this method, and in general these acid extractions will have few advantages over the more formal approaches.

A rather unusual method for the determination of gold was used by Caley[52] for alloys of high gold content. Its special value for the determination of gold in valuable objects is evident. The method involves the determination of the density of the object and the application of the tea-mixing rule, and depends upon the high density and content of gold, the assumption that the gold is mechanically mixed, a reasonably accurate knowledge of the qualitative composition of the object and other data. In favourable cases the accuracy of the determination can be quite high. The method will have an excellent application in naturally occurring quartz containing gold nuggets.

METHODS FOR CYANIDE-GOLD SOLUTIONS

Because of the extensive industrial applications of cyanide solutions for the extraction of gold from ores the analytical methods applied to these solutions will be discussed collectively. Although the number of pertinent publications during the past four decades is large, few outstanding innovations have been introduced into the older methods. One of the most widely used of the older procedures was developed by Chiddy,[53] and according to Bugbee[54] "is used almost exclusively in this country for the assay of cyanide solutions. It works equally well on strong or weak, foul or pure solutions, and almost any quantity may be taken". The method involves addition to the cyanide solution of lead acetate-acetic acid solution and fine zinc shavings or zinc emulsion. Finally hydrochloric acid is added to the hot solution to remove excess zinc. The supernatant liquid is decanted, and the sponge is pressed into a compact mass and cupelled.

Wogrinz[55] rejected the Chiddy method when the cyanide solutions contained ferrocyanide, but this, however could be destroyed by evaporation to a residue, and then fuming with sulphuric acid. After treatment with *aqua regia*, hydrochloric acid, lead acetate and zinc powder, the gold was collected, washed, ignited and weighed. Roodhouse[56] modified the Chiddy method slightly by adding acetic acid to the reduced mixture, followed by boiling, decantation and addition of hydrochloric acid. Bugbee[54] stated that "the Chiddy method with its numerous modifications is reported to be unpopular on the Rand on account of the care required if satisfactory results are to be obtained and because it requires the application of heat". The alternative procedures, used in the absence of thiocyanates, involve the addition of copper^{I} chloride in hydrochloric acid or the production of copper^{I} ion *in situ* by adding consecutively a saturated solution of sodium cyanide, copper sulphate, sodium sulphite and sulphuric acid. Potassium ferrocyanide is added in small amounts to provide a carrier and to aid in filtering. With the last two methods the gold is first precipitated as $CuAuCn_2$, and the excess cyanide removed as copper^{I} cyanide. The precipitation is accomplished in the cold. The use of potassium ferrocyanide as a coagulant was rejected by Creed and Cayton-Boxall[57–59] as unnecessary and leading to losses when excess is present. King and Wolfe[60] provided an improved copper^{I} chloride procedure which required the use of the ferrocyanide as a coagulant, and the authors cautioned against the presence of an excess. The precipitate and filter were subsequently fire-assayed.

To avoid the necessity of destroying cyanide before determining gold, Bettel[61] used a zinc-copper couple obtained by adding to a strong cyanide solution copper^{I} cyanide and zinc fume. For approximate work colorimetric methods were used, but for accurate analysis the precipitated gold was freed from zinc and organic matter. In a later publication Bettel[62] followed the copper^{I} chloride precipitation by a treatment of the fitrate with zinc and lead acetate in excess hydrochloric acid. In 1934, Ageenkov *et al.*[63] stated that the recorded methods for sampling and analysing cyanide solutions yielded very inaccurate results.

A wide variety of reducing reagents have been proposed for the reduction of gold salts in cyanide solutions. Bayula[64] used carbon, and subsequently fire assayed the precipitate. For the determination of gold in cyanide plating solutions, Kushner[65] rejected the classical reduction methods for routine purposes because of the excessive time and the tedious techniques required, and the sulphuric acid evaporation method because of a tendency toward the formation of colloidal gold and of the poisonous fumes evolved during the heat treatment.[66,67] The method proposed by him included the removal of free cyanide by the addition of silver nitrate and subsequent fuming with sulphuric acid. Methods such as these are far from specific. The noble metals and associated base metals interfere, although slight modifications could be applied to ensure satisfactory recoveries.

Nitric acid was used by Marenkov[68] to isolate gold in cyanide slimes, subsequently dissolving it in *aqua regia* and re-precipitating by hydrazine hydrochloride. Seath and Beamish[30] used zinc in mill-cyanide solution to precipitate gold, tellurium and silver collectively; the mixture was then dissolved and treated with hydroquinone to remove gold selectively. Shah[69] also used zinc, the excess being removed in a sulphuric acid solution. The gold was purified by nitric acid before weighing. Rochat[70] used aluminium foil to isolate gold, which was then purified by nitric acid within an error of 0·5%. Aluminium sheet has been used in a modification of the Chiddy method.* After the removal of lime by sodium hydroxide and filtration, the sheet is completely immersed. The resulting sponge is coherent and relatively free from impurities. Presumably the method requires the presence of silver. The chemical explanation of the procedure presents an interesting problem.

The simultaneous precipitation of gold and mercury has been used as an analytical method. Thus Caldwell and McLeod[71] treated a "simulated cyanide solution" with a large excess of ferrous sulphate to convert the cyanide to ferrocyanide, then mercuric chloride solution and magnesium powder and concentrated hydrochloric acid. After standing overnight the mercuric-gold mixture was decanted and filtered, lead was added, and the gold was isolated by cupellation. It is surprising that the author offers no comment concerning the possibility of gold losses in the presence of potassium ferrocyanide, since such a loss has been emphasised by assayers,[60,72] who recommended only very small amounts of ferrocyanide to provide a carrier in the copper^{I} chloride method. While the results provided by Caldwell and McLeod, by Smith[72] and particularly by Wogrinz[55] (who stated that the method of Chiddy[53] was inapplicable in the presence of ferrocyanide) indicate low recoveries, the values are quite comparable to those recorded for the older-established procedures. Obviously there is here a problem of some practical significance. The mercury-gold collection was also used by Lundquist[73] who treated the cyanide solution with zinc dust, and then with mercuric chloride. After warming of the solution, hydroxylamine hydrochloride and ammonium hydroxide were added and the excess zinc was dissolved by hydrochloric acid. The gold amalgam was treated with nitric acid to remove all traces of mercury, and the zinc was then annealed and weighed. Wilson[74] provided elementary details for the determination of gold in cyanide solutions by ferrous sulphate and oxalic acid, after elimination of hydrogen cyanide by hydrochloric acid. Precipitation by zinc was discussed, and a method was proposed which involved evaporation of the cyanide solution to a syrup, addition of litharge, evaporation to dryness, and heating the residue to form a button. The lead was selectively parted by nitric acid. Cadmium sulphide powder has been used to precipitate gold sulphide from an acidified solution of cyanide electrolyte.[75] The precipitate was then ignited, treated with nitric acid and finally converted to gold at 800–900°.

TITRIMETRIC DETERMINATIONS

Most of the titrimetric procedures for gold require a precipitation of the metal or of the aurous salt. In all but the iodometric gold methods, the end-points are determined through potentiometric techniques or by back-titrations against excess of reductant. As would be expected from the reduction potentials of gold salts, there is available a wide variety of reducing agents. Among the most suitable are hydroquinone, iron^{II}, arsenite ion and ascorbic acid. Others of use for specific purposes, but not recommended for general use, are titanium^{III}, tin^{II}, chromium^{II}, copper^{I}, hydrazine salts, sulphur dioxide, *etc.*

Potassium iodide is a notable exception to the general type of reductant involved

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* Private communication from S. E. Wolfe.

in gold titrations. One of the earliest reagents, it was used in 1899 by Peterson,[76] who suggested that the reaction resulted in the stoichiometric formation of univalent gold iodide and free iodine, the former reacting with sodium thiosulphate to produce $NaAuS_2O_3$. Thus Peterson believed that the quantitative relationship was one atomic weight of gold to three formula weights of sodium thiosulphate. Whether or not the above gold complex is formed, there can be little doubt that the proposed equation is unacceptable. In any case, Gooch and Moreley[77] indicated that the relationship of gold to iodine is 1:2, and found "no evidence whatever" for the reaction to form $NaAuS_2O_3$. These authors used amounts of gold of the order of 1 mg or less, and recorded that the reaction was influenced by the "volume of the solution, the mass of iodine present, and the time of action". To avoid the presence of foreign oxidising substances during the dissolution of gold by chlorine water or *aqua regia*, the solution was twice treated with ammonia in excess, boiled, and acidified with hydrochloric acid. The titration procedure involved the addition of excess potassium iodide just sufficient to dissolve the gold-iodide. The liberated iodine was titrated with standard sodium thiosulphate to a clear solution in the presence of starch and then standard iodine was added to the rose-coloured end-point. Excellent results were obtained with $0{\cdot}01N$ or $0{\cdot}001N$ solutions of the titrant, and in general the work of these authors reaches a high standard. Scott[78] records the above method for small amounts of gold, but, without explanation, recommended the determination of an experimental gold factor for the standard thiosulphate solution.

For larger amounts of gold the Gooch and Morley method has been found inapplicable. Rupp[79] ascribed the difficulty to the instability of gold^{I} iodide, which slowly dissociated into gold and iodine. Herschlag[80] rejected the suggestion that the instability of gold^{I} iodide was a main cause of error, and without sufficient experimental evidence he claimed that the error was caused "by a side reaction involving the aurous iodide complex and thiosulphate". This statement was made as a result of Lenher's[81] ability to obtain accurate results on samples of gold ranging from 0·0395 to 0·7301 g by a titration of released iodine with a standard sulphurous acid solution, in which the back-titration with iodine used by Gooch and Morley was not required. Vanning and Hartwagner[82] rejected Peterson's method because the calculations based on the assumption of one formula weight of gold to three of sodium thiosulphate produced high experimental results; and they rejected Gooch and Morley's method because of inaccuracy which became more evident when larger amounts of gold were used. The proposed method depended upon the oxidation of excess potassium iodide by $6AuCl_3{\cdot}HCl$ to produce 12I and 6HCl, the latter producing 6I in a solution containing potassium iodide and iodate, a final relationship of 18I to 18 formula weights of sodium thiosulphate. The results obtained in pure $HAuCl_4$ solution were an improvement on those from older methods, but the method will have a very limited application since acids other than the combined hydrogen chloride are inadmissible. Unfortunately these authors' report[82] included no reference to the preparation of gold solutions by dissolution of the metal.

Herschlag[80] recorded one of the most acceptable iodide procedures. Here the interference from the nitric-hydrochloric acid dissolution of the gold was removed by treating with sodium hypochlorite or by potassium chlorate, diluting and boiling out the excess chlorine. The solution was then neutralised with sodium carbonate, slightly acidified and made basic to litmus with sodium hydrogen carbonate. Unlike in the earlier treatment with ammonia, no precipitate appeared during this neutralising process. Excess potassium iodide was added rapidly to avoid the oxidation of iodine by gold^{III} chloride, and the liberated iodine was titrated with standard 0·01N sodium arsenite. The latter was standardised by iodine, and the gold content was calculated stoichiometrically. The method was applied to pure gold solutions, gold in cyanide solutions and gold solutions containing copper, iron, silver and nickel. Interference occurred when the coloured precipitates in the basic medium interfered with the starch end-point. The colour of platinum and palladium iodide complexes also caused some interference. The recoveries on samples of 20–400 mg of gold were exceptionally accurate. The above procedure has been recommended by Young[83] who reviewed various titrimetric methods for gold.

With the exception of Peterson's explanation[76] for the gold iodide reaction there has been general agreement that the ratio of reactants is one atomic weight of gold to two atomic weights of iodine. In all cases excess of potassium iodide has been used in both acid and basic solutions of gold^{III} chloride. However, Brull and Griffi[84,85] have applied successfully a procedure based on the reaction:

$$2AuCl_3 + 6KI = 6KCl + Au(AuI_4) + I_2 \qquad (1)$$

rather than the generally accepted reaction:

$$AuCl_3 + 3KI = 3KCl + AuI + I_2. \qquad (2)$$

Inexplicably, the experimental results which have been recorded for both relationships have been quite acceptable. Brull and Griffi recommend their method for quantities of gold of the order of 1 to 2 mg. With about 10 mg there was some indication that the reaction (2) became effective. Variation in the proportion of potassium iodide appeared to be without effect. Attempts to isolate the complex $Au(AuI_4)$ failed. The authors found that copper did not interfere[85] provided that the excess of potassium iodide was not too great. It is unfortunate that the publications dealing with this important iodometric method contain insufficiently complete information concerning the influence of acidity, iodide concentration, optimum amounts of gold, *etc.* The provision of the information which is lacking would be a useful contribution.

Parker[86] used a method somewhat similar to Herschlag's to determine gold in plating solutions containing nickel and copper. However, cyanide was eliminated by treatment with nitric and hydrochloric acids and nitrite with sodium hypochlorite. There was no interference from iron^{II}, iron^{III}, zinc, stannate^{II}, nickel, silver, copper^{I} or copper^{II}. Sudilovskaya[87] rejected the mixed acid method for the elimination of cyanide interference, and recommended treatment by repeated evaporations, fusion with metallic sodium and treatment with concentrated sulphuric acid.

An unusual back-titration was proposed by Lespagnol and Merville,[88] who precipitated gold by formaldehyde and treated the precipitate in a hydrochloric acid medium with standard 0·1N iodine and a solution of potassium iodide. The excess iodine, residual from the dissolution of gold^{I} iodide, was titrated with 0·1N sodium thiosulphate. The method was applicable to medicinals, *etc.*

A unique iodometric method, and one worthy of further attention, was recently described by Riolu and Garrini[89]. These authors treated solutions of 1–7 mg of gold^{III} salt with an excess of 0·01M sodium chlorite. The stoichiometrically formed chlorine dioxide was swept from the mixture by carbon dioxide over a period of 1 hour or more and collected in a solution containing sodium iodide and hydrochloric acid. The liberated iodine was titrated with sodium thiosulphate. There was no interference from silver, copper, zinc, nickel, iron, platinum and cadmium. The error was less than 1%. Someya[90] used potassium iodide to titrate gold^{III} chloride in slightly acid solution potentiometrically. The first discontinuity was the result of reduction of the chlorine used to oxidise the gold to the tervalent state; this was followed by the discontinuity due to gold^{I} iodide. Copper did not interfere. The author discussed the potentiometric methods for selenium, tellurium and gold.

An interesting application of the gold iodometric determination was described by Murray and Krige[91]. In an attempt to find a wet method for the gold assay of ores these authors digested the sample with bromine water or *aqua regia*. The filtered solution was finally titrated potentiometrically with 0·01*M* potassium iodide using saturated calomel and platinum wire electrodes with a potassium chloride-agar bridge. The end-point was accepted as the maximum value of the ratio of voltage to volume of titrant. For various reasons only very small concentrations of hydrochloric and nitric acids were admissible. This method may find useful application to a restricted type of ore, but because it is time-consuming and subject to a variety of interferences it is not recommended for application to gold ores in general. While the results agreed fairly well with the classical assay the method was not recommended as a substitute.

Precipitating reductimetry

Organic titrants: Derivatives of aminophenols are among the most effective reducing reagents to be applied titrimetrically. In a series of papers Pollard described their application to both large and small amounts of gold. The earliest procedure[92] was designed primarily for amounts of gold of 5 mg or less, and involved dissolution of gold in small amounts of *aqua regia*, boiling and removal of nitrosyl chloride and chlorine by paraldehyde assisted by air blown through the solution. After dilution of the solution, the gold ion indicator *o*-tolidene was added, followed by silver nitrate as a catalyst, and the titration was carried out with standard "Metol". Except that small amounts of copper could be tolerated, no information was provided concerning the interference of associated metals.

Before the above publication, Pollard[93] in response to a demand for a rapid inexpensive method for "hall marking", developed a titrimetric method for larger amounts of gold. It is surprising that this mercurous titration, a relatively objectionable method, was preferred to the iodide or the iron^{II} reduction, both of which had been recorded more than a decade earlier. While Pollard makes no reference to the earlier methods it is interesting that the proposed procedure involved the iodide reduction. The new method required dissolution in warm *aqua regia*, and the passage of air to eliminate reducing gases. Urea was added to remove nitrous acid, and potassium bromide to accelerate reduction of gold^{I} salt and to form the brown bromoauric acid which was reduced by standard arsenious acid. The latter was made with hydrochloric acid, and contained mercuric chloride and a small amount of potassium iodide. The gold^{III} salt liberated iodine which reacted immediately with the arsenious acid. The reverse reaction, through the action of iodide ion, was prevented by the formation of $HgCl_2.HgI_2$. Furthermore, the iodide concentration was thus kept sufficiently low to prevent interference from other metals except thallium, palladium and iridium. An amount of the standard arsenic solution almost sufficient to precipitate the gold, as indicated by the disappearance of the brown bromoauric acid, was added. The final trace of the latter was determined by the addition of *o*-tolidene or dianisidine indicator, containing sodium fluoride to complex the iron, and the titration was completed with standard hydroquinone. The results from known gold samples indicated a high degree of accuracy. There was no interference from large amounts of copper, nickel and iron, or from small amounts of lead, zinc, platinum and various other metals. Palladium and ruthenium interfered. The author offers a fair summary of the applicability of the method in that for "hall marking" there would be considerable economy of time and cost as compared to the furnace assay. For general purposes there are objections in that the liquid to be titrated is a mixture with gold and the end-point is thus obscured. Furthermore, two standard solutions are required. In any case the direct titration with arsenic^{III} in a basic medium[80] is simpler and of more general application.

Pollard[94] recorded one of the most useful titrimetric methods for micro amounts of gold. Precipitated gold was dissolved from the filter by bromine water acidified with hydrochloric acid. *Aqua regia* could also be used. Interfering gases were removed by impinging air on the surface of the gold solution. After dilution, the solution was buffered with potassium fluoride, *o*-dianisidine was added, preferably near the end-point, and the gold was titrated with hydroquinone solution. There was no appreciable interference from the associated base metals, copper, silver, iron and nickel. The method was best suited for 2 mg of gold or less; for very small quantities, the gold was initially co-precipitated with tellurium by reduction with sulphur dioxide gas. This precipitation was used successfully for the recovery of gold at a dilution of one part in a thousand million parts of solution. The method was found suitable for the determination of gold in urine. For this determination Jamieson and Watson[95] used a modification of Pollard's method. Samples of urine containing 0·085–0·522 mg of gold were used, and the addition of sodium chloride to assist coagulation and subsequent boiling were required for acceptable recoveries.

Zvyagintsev and co-workers[96,97] used the hydroquinone titration for gold-cyanide solutions. After treatment with nitric acid and potassium chlorate, the solution was adjusted with caustic solution to a slightly acid reaction and then titrated with hydroquinone. The hydroquinone titration was used by Zharkova and Zhaeheva[98] to determine gold in cyanide electrolytes. The solution was neutralised and gold was separated by hydrazine hydrochloride, then redissolved, and finally titrated with hydroquinone in the presence of potassium bifluoride and *o*-dianisidine. The relative value of indicators for the hydroquinone titration was discussed by Belcher and Nutten[99]. Of those examined, 3-methylbenzidine gave the best colour change. End-points with benzidine and 2,7-diaminofluorone were sharper than those obtained with *o*-dianisidine whose change from red-violet to violet was difficult to determine. The authors also discussed the effects of acid strength and time on the colour change of indicators. Milazzo[100] used the hydroquinone titration after a carrier precipitation with copper or lead by hydrogen sulphide or sodium sulphide. The combined sulphides were roasted and the copper selectively removed by sulphuric acid. The gold was dissolved in *aqua regia* and the solution was evaporated with hydrochloric acid to remove oxides of nitrogen. Potassium hydrogen fluoride was added and the gold was titrated with hydroquinone in the presence of *o*-dianisidine. Iridium interfered, and under certain conditions the colours of platinum and rhodium salts interfered with the detection of the end-point. The author's claim of superiority over existing methods is not justified. In the present author's opinion the collective precipitation with copper and its subsequent selective dissolution invites greater error than the co-precipitation method with tellurium, proposed by Pollard[94]. Concerning the question of interfering elements, the author has too readily predicted *a priori* the degree of interference from published oxidation-reduction potentials.[101] In any case the description of the experimental results on interferences indicates an inadequate approach.

Various potentiometric titrations have been proposed. Ryabchikov and Knyazheva[102] used a gold wire electrode, in a slightly acid solution of gold freed from nitric acid by evaporation with hydrochloric acid, and titrated the hot solution with hydroquinone or Mohr's salt in a current of carbon dioxide. Of the platinum group only iridium interfered. Czaplinski and Trokowicz[103] used platinum and calomel electrodes with a similarly treated gold solution, and titrated at a pH of 2–5 with a 0·01N hydroquinone solution. The potential change at 50°, at the equivalence point, after adding one drop of the titrant, was above 100 mV. Copper and platinum did not interfere. Reishakhrit and Sukhobokova[104] used a rotating platinum electrode and 2N sulphuric acid as an auxiliary electrolyte. The hydroquinone titration was carried out at 60° at a potential of 1 volt in relation to a standard calomel electrode. Palladium did not interfere.

Ascorbic acid has proved to be a useful titrant for gold. Stathis and Gatos[105] used an excess of the standard reagent, and a gold solution containing hydrochloric acid but free of oxidising constituents, and titrated the excess with iodine solution. The results were excellent, and copper did not interfere. No references were made to other interferences. Erdey and Rady[106] developed a potentiometric method with ascorbic acid as the titrant. The gold^{III} solution was maintained at 50°, the acidity at pH 1·6–3, and the chloride concentration at a maximum of 0·1N. The end-point was readily discernible, and the accuracy of the method was about $\pm 1\,\%$ with 0·01N solutions. There was no interference from mercury^{II}, copper^{II} or iron.^{III} Platinum^{IV} caused high results. Both ascorbic acid methods are recommended.

Hydrazine sulphate has also been used for the potentiometric determination of as little as 0·1 mg of gold in 0·01–0·001M hydrochloric acid.[107] Franceschi[108] used potassium oxalate to precipitate gold and back-titrated the excess with potassium permanganate.

***Reduction by metal salts*:** The very early titrimetric methods included reduction of gold^{III} salts to gold by standard iron^{II} salts, and back-titrations with potassium permanganate. Thus in 1878, Juptner[109] determined gold in alloys after dissolution in *aqua regia* and boiling to remove oxidising gases.

In 1913, French[110] discussed the new titrimetric methods recently introduced into Mints. One procedure involved the determination of gold by reduction with Mohr's salt in sulphuric acid solution, and titration of the excess with potassium permanganate. Tsobar[111] used the method for gold alloys containing copper. The hydrochloric acid solution, free of oxides of nitrogen, was neutralised with sodium hydrogen carbonate to the formation of an amorphous precipitate. It was then slightly acidified with sulphuric acid and titrated with potassium permanganate. The method remains one of the most acceptable for the titrimetric determination of gold, and appropriate procedures are recorded in modern textbooks.[78] Iron^{II} reduction has also been used, the end-point being indicated potentiometrically. Moller and Weisbrod[112–114] have thus determined gold from both a hydrochloric acid and a nitric acid medium. To ensure complete conversion to gold^{III}, chlorine was added, in which case only the second inflection corresponded to the reduction of the gold salt. In the presence of nitric acid[112,114] the latter inflection was less abrupt, but the addition of alcohol and potassium sulphate provided some improvement. Platinum and palladium interfered.

Titanium^{III} chloride has also been used for the potentiometric determination of gold. As compared with iron^{II} salts, there is the disadvantage of relative instability in air. Zintl and co-workers[115–117] used a hydrochloric acid solution and potassium bromate to ensure oxidation of gold^{I} salts. Zintl[118] also provided a potentiometric titration with chromium^{II} chloride. Tervalent gold, bivalent copper and univalent mercury could be titrated in succession. The gold was dissolved in 2–5% hydrochloric acid, and bismuth chloride was added as a catalyst. Gold salts alone produced high results through the catalytic decomposition of chromium chloride by metallic gold. This was prevented by copper ion.

Vanadyl sulphate has also been used for potentiometric titrations. Del Fresno and Mairlot[119] used strongly alkaline gold solutions above 50°.

Muller and Tanzler[120] used copper^{I} chloride, whose stability was acceptable if air was excluded. Chlorine was added to ensure complete conversion to $AuCl_4^-$, which was reduced by copper^{I} to gold. Solutions containing both platinum^{IV} and gold^{III} could be titrated. Lingane[121] developed a coulometric titration of gold, in which the $CuCl_2^-$ was generated electrolytically from a supporting electrolyte of 0·04M copper^{II} sulphate in 1–2M hydrochloric acid solution, with a generator cathode of pure gold and a generator anode of cadmium metal in an anolyte of cadmium chloride in potassium chloride. Air was removed by a current of nitrogen, and the equivalence-point was detected potentiometrically with gold-saturated calomel electrodes. Gold was reduced stepwise first to $AuCl_2^-$, then to gold. There was some evidence that nitrate ion at a concentration of 0·02M did not interfere. Thus it would seem that the author need not have evaporated the gold solutions with hydrochloric acid. Samples of gold in the range of 1 to 100 mg were titrated with an average error of ±0·3%. It is significant that there exists the possibility of titrating 100 micrograms of gold within an error of ±1%. A large amount of platinum, more than half that of the gold, produced positive errors; small amounts were without effect. Large amounts of copper, silver, mercury and lead did not interfere. The author's statement that "since lead does not interfere, the titration is applicable to the lead-gold alloy obtained by fire assay methods, provided platinum group metals are not present" is unacceptable. Aside from the fact that almost any classical method for a metal can be made applicable irrespective of the associated metals, the author's claim makes no recognition of the fact that the dissolution and preparation for the proposed coulometric titration of a 25-g lead button containing a milligram or so of gold would be no simple procedure. Furthermore, if the lead is removed by cupellation, it is unlikely that an experienced chemist would choose lengthy procedures when simple weighing is sufficient. The proposed coulometric method can be useful for specific purposes, but it is not recommended for general use.

With the exception of iron^{II} none of the transition metals' salts is recommended as titrants; most of them lack stability in air and all of them involve amperometric or potentiometric techniques. This objection applies also to the tin^{II} reduction. Muller and co-workers[122,123] have used this method for gold and platinum, in an atmosphere of nitrogen. When both of these metals are present the one end-point represents complete precipitation of both metals. Tin^{II} chloride was also used by Hirano[124] as a titrant, with the end-point indicated photometrically. A clear break in the developing purple colour appeared, provided that the acidity of the solution was kept below 0·05N and excess chlorine was present. There was no interference from small amounts of copper, lead and iron. Because so many simpler methods are available this technique has little to recommend it. An interesting coulometric method involving electrogenerated tin^{II} was described by Baird and Lingane.[125] The optimum supporting electrolyte was 3–4M sodium bromide, 0·3N hydrochloric acid and 0·2M tin^{IV} chloride. A gold generator cathode was used. The solution was de-aerated with nitrogen. The reduction proceeded from $AuBr_4^{2-}$ to gold. The end-point could be observed amperometrically through the use of two small, identical, gold electrodes maintained at 100 to 200 mV. The titration could also be followed spectrophotometrically at a wavelength of 400 mμ. In contrast to the amperometric and potentiometric methods, the spectrophotometric procedure indicated only the reduction to $AuBr_2^-$. With the first two methods, and 0·5–23 mg of gold, the average error was ±0·3%. With the last the average error was about 2%. Interference from other metals was not investigated.

A unique titrimetric method for the determination of colloidal gold involves a titration with standard potassium cyanide. Wagner[126] used an adaptation of the method for the determination of gold in cyanide solution. The latter was evaporated to fumes with sulphuric acid to produce metallic gold, which, after dissolution in *aqua regia*, was treated with ammonia. Standard potassium cyanide was added, and the excess over that required to dissolve the gold precipitate was titrated with silver nitrate, with potassium iodide as an indicator. For the direct determination of gold sols produced by a variety of methods, Pennycuick and Woolcock[127] used a standard potassium cyanide solution. At a pH above 7, 8 moles of potassium cyanide reacted with 2 formula weights of gold.

A direct determination of gold by titration with 0·1N sodium arsenite was developed by Szebelledy and Viczian.[128] The chloride solution was treated with sodium bromide, and the red $AuBr_4^-$ ion was titrated at 90° in the presence of gelatin, which prevented reduction to metallic gold. The arsenite reduced the red auric bromide to colourless $AuBr_2^-$. The method suffers from a large variety of metal interferences, and the end-point is not obtained without some difficulty. Better methods are available. In the author's opinion this statement also applies to certain of the titrimetric methods proposed by Lenher.[81] These procedures require the reduction by a standard sulphur dioxide solution of gold^{III} chloride containing magnesium chloride and potassium bromide, or magnesium chloride alone, or sodium chloride. The author quotes very acceptable results, but in this case there is the problem not only of interferences and uncertain end-points, but also of the instability of the reducing reagent. It is interesting to note that whereas the titration results in a reduction to univalent gold, the reagent sulphur dioxide is used satisfactorily as a precipitant for gold. As far as the present author knows, little has been recorded concerning the interference of alkali metal and alkaline earth salts with the precipitation of gold by sulphur dioxide.

Methods for gold have been included in the large number of heterometric titrations developed by Bobtelsky[129] and associates. To determine gold alone, the method recommended involves the titration with nitron of a solution containing about 1 mg of gold, potassium thiocyanate and either dilute or concentrated ammonia. With the former the white compound AuN appeared, and with the latter the yellow Au_2N_3 was formed. Procedures were provided for determining gold in mixtures of palladium and platinum. The titration required 5–10 minutes and the error was between 0 and 1%. The publication quoted contains informative material, potentially useful in both titrimetric and gravimetric areas.

Zusammenfassung—Die Ubersicht enthält die einschlägige Literatur bis Juli 1960. Es wurde versucht die im allgemeinsten anwendbaren titrimetrischen und gravimetrischen Methoden zur Bestimmung von Gold herauszufinden. Wenngleich einige Methoden unter diesem Gesichtpunkte abgelehnt werden mussten, soll zugegeben werden, dass sie unter Bedingungen, wo zahlreiche Proben zu analysieren sind und einigermassen konstante Bedingungen vorwalten, von grossem Nutzen sein können. Wegen ihrer weiten Anwendbarkeit wird die Methode, Gold aus cyanidhaltiger Lösung zu fällen, separat behandelt. Die zahlreichen Widersprüche, betreffend die iodometrische Methode der Goldbestimmung wurden betont.

Résumé—Cette étude comprend toute la littérature appropriée publiée avant juillet 1960. L'auteur a essayé d'identifier les méthodes titrimétriques et gravimétriques les plus généralement applicables pour le dosage de l'or. Alors que certaines méthodes ont été rejetées pour cette raison, on admet que si de nombreux dosages sont faits et que les compositions qualitatives sont à peu près constantes, certaines de ces méthodes peuvent être particulièrement efficaces. A cause de son application étendue, la précipitation de l'or en solution de cyanure est traitée séparément. Le caractère controversé de la méthode iodométrique pour l'or a été souligné.

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THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—V

THE DETERMINATION OF CADMIUM

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Summary—A method is described for the determination of cadmium in beryllium or beryllium oxide. Cadmium is precipitated with benzotriazole using nickel as a carrier. A further separation from other elements is made by passing a chloride solution through Dowex-1 anion-exchange resin. The cadmium is finally determined with dithizone. The method is accurate to ±5% or 0·4 μg of cadmium, whichever is greater. No interference is caused by the presence of 10-mg amounts of 68 elements.

INTRODUCTION

A METHOD for the determination of cadmium in beryllium or beryllium oxide is presented which is specific within the limits investigated. No interference is caused by at least 10-mg amounts of 68 elements. The presence of greater than 100 μg of zinc necessitates a minor modification of the method. The presence of zinc in greatly interfering amounts can be recognised by the red colour of the aqueous phase during the dithizone-chloroform extraction.

The method is based on the precipitation of cadmium from an ammoniacal citrate solution with benzotriazole, using nickel as a collector.[1] A 10% hydrochloric acid solution containing cadmium and other elements precipitated with benzotriazole (zinc, copper, cobalt and nickel) is passed through a column containing Dowex-1 anion-exchange resin. Cadmium and zinc are retained by the resin and are subsequently eluted with 3*M* nitric acid. Cadmium is then extracted from a strongly alkaline medium with a chloroform solution of dithizone.[2] The absorbance of this extract measured at 518 mμ is a linear function of the cadmium concentration, at least between 0·05 and 1·0 μg of cadmium per ml. The colour is stable in diffuse light for at least 24 hours.

EXPERIMENTAL

Apparatus

Beckman DU spectrophotometer: With 1-, 2- and 5-cm cells.

Ion-Exchange columns: 1 cm I.D., 12 cm long, containing 8 cm of Dowex-1, 200–400 mesh, 8% crosslinkage.

Reagents

Distilled water was used throughout.

Standard cadmium solution: Dissolve 100 mg of pure cadmium metal in 1 ml of nitric acid. Add 1 ml of sulphuric acid and evaporate to near dryness. Cool and dilute to 1 litre. Dilute this solution to obtain a solution containing 1 μg of cadmium per ml.

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* Part IV: *Talanta*, 1960, 5, 250.

Nickel solution: Dissolve sufficient nickel chloride, nitrate, or sulphate to obtain a solution containing 5 mg of nickel per ml.

Nitric acid, 16*M* and 3*M*.

Citric acid, 50% (w/v).

Sulphuric acid, 18*M*.

Benzotriazole, 2% (w/v) aqueous solution: Prepare fresh solution by adding hot water to a weighed amount of the solid material.

Ammonium hydroxide, 12*M*.

Perchloric acid, 70%.

Hydrochloric acid, 12*M* and 1·2*M*.

Tartaric acid, 2% (w/v).

Hydroxylamine hydrochloride, 5% (w/v).

Sodium hydroxide, 40% (w/v), containing 0·05% (w/v) potassium cyanide.

Dithizone solution, 10–15 mg in 1 litre of chloroform: Purify the dithizone solution in the usual manner,[3] and adjust the dithizone concentration by appropriate dilution of the purified material, using the reported molar absorptivity, 41,500 at 605 mμ.[4]

Procedure

Transfer a sample containing approximately 10 μg of cadmium to a 600-ml beaker. Dissolve beryllium oxide in hot 6*M* sulphuric acid (20 ml per g of oxide). Dissolve beryllium metal by suspending the sample in water and gradually adding hydrochloric acid (10 ml per g of metal). When the reaction ceases, add a few drops of 30% hydrogen peroxide if necessary, to dissolve any remaining particles of unoxidised metal. Heat to destroy the excess peroxide.

If the sample was dissolved in 6*M* sulphuric acid, add 10 ml of hydrochloric acid. If the sample was dissolved in hydrochloric acid, add 20 ml of 6*M* sulphuric acid. Dilute to about 150 ml with water, add 5 ml of the nickel solution and sufficient 50% citric acid to complex the beryllium (25 ml per g of beryllium), and adjust the pH to 8·25 ± 0·1 with ammonium hydroxide. Dilute to about 300 ml with water. Add 25 ml of 2% benzotriazole solution and digest on a steam bath for 2 hr. Allow the precipitate to stand overnight at room temperature. Add filter pulp, filter through Whatman-40 filter paper, and wash with a minimum amount of a 1% ammonium citrate solution previously adjusted to pH 8·25.

Transfer the paper to the original beaker, add 25 ml each of nitric acid and perchloric acid, evaporate to fumes of perchloric acid and finally to dryness.

Dissolve the salts in 100 ml of 1·2*M* hydrochloric acid, warming if necessary, and cool to room temperature. Pass this solution through the anion-exchange resin (which has previously been washed with 100 ml of 3*M* nitric acid, then 100 ml of water, and finally, converted to the chloride form with 100 ml of 1·2*M* hydrochloric acid) and wash the resin with about 10 column volumes (about 200 ml) of the same acid, discarding the eluate.

Elute the cadmium by passing 125 ml of 3*M* nitric acid through the column. Add to the eluate 1 ml of sulphuric acid and evaporate to dryness. Dissolve the salts in water.

Transfer the solution, or an aliquot containing a maximum of 10 μg of cadmium, to a 125-ml separatory funnel. Add in the following order, swirling after each addition, 25 ml of 2% tartaric acid, 1 ml of 5% hydroxylamine hydrochloride, 5 ml of 40% sodium hydroxide—0·05% potassium cyanide solution and 20 ml of dithizone solution. Shake for 1 min, insert a little cotton in the stem of the funnel and filter the chloroform layer into a 1-, 2- or 5-cm cell. Measure the absorbance of the pink extract at 518 mμ, using chloroform as a reference. Determine the cadmium concentration by reference to a standard curve obtained by carrying known amounts of cadmium through the dithizone extraction procedure. A blank and at least one standard should be carried through the entire procedure.

Precipitation of nickel with benzotriazole and collection of cadmium

Precipitation of copper with benzotriazole is carried out at a pH of 7·0–8·5.[2] Iron^{II}, silver, nickel, cadmium, zinc and cobalt ions give similar precipitates, but the optimum pH for precipitation is not given. In our investigation we attempted to ascertain the optimum pH for quantitative recovery of cadmium as the benzotriazole compound by co-precipitation with nickel. Table I indicates that cadmium is quantitatively recovered at a pH of 8·0–8·5.

The experiments described in Table I were an attempt to determine the optimum pH for precipitation under several conditions. The effect of beryllium oxide, sulphuric acid, and citric acid was investigated at several pH values.

The table is self-explanatory, indicating that at a pH of 7·5 reasonably good recovery of cadmium is obtained from a water solution, whereas the presence of sulphuric acid leads to slightly low results. The presence of citric acid leads to very low results. However, the presence of beryllium, which forms a complex with citrate, leads to much better recovery. Excellent results are obtained under all of the conditions tested at a pH of 8·0 to 8·5. Consequently, a pH of 8·25 is recommended.

TABLE 1.—RECOVERY OF CADMIUM BY CO-PRECIPITATION WITH NICKEL

BeO, *g*	H_2SO_4, mmoles	Citric acid, *g*	pH	Cd recovered, %
0	240	20	7·5	54,72
0	120	0	7·5	91,92
0	240	0	7·5	90
0	360	0	7·5	88,92
0	0	0	7·5	93
0·5	270	20	7·5	58,29
0·5	60	5	7·5	98
1·0	300	20	7·5	78,80
1·0	120	10	7·5	104
1·5	330	20	7·5	95
2·0	360	20	7·5	99,99
2·0	240	20	7·5	100
0	240	20	8·0	100,98
0	0	0	8·0	101
0·5	270	20	8·0	99
0·5	60	5	8·0	101
1·0	300	20	8·0	98,99
1·0	120	10	8·0	102
1·5	330	20	8·0	99
2·0	360	20	8·0	100,98
2·0	240	20	8·0	105
0	240	20	8·25	99,97
1·0	300	20	8·25	100,100
0	240	20	8·5	99
0·5	270	20	8·5	99
1·0	300	20	8·5	101,101
1·5	330	20	8·5	101
2·0	360	20	8·5	100
0	240	20	9·0	99,100
0·5	270	20	9·0	92,97
1·0	300	20	9·0	93,95
1·5	330	20	9·0	98
2·0	360	20	9·0	96,98

[a] 12·5 μg of cadmium added. Ten ml of 12*M* HCl present in all cases

Extraction and measurement of the cadmium-dithizonate complex

The amount of dithizone specified in the above procedure is adequate for up to 24 μg of cadmium. If the absorbance of the sample indicates a higher cadmium content, a smaller aliquot of the sample solution is recommended. If no more sample solution is available, a second, and, if necessary a third extraction with fresh portions of dithizone should be made and the chloroform solution treated as described for the separation of cadmium from excessive amounts of zinc.

The colour of the cadmium dithizonate is stable in diffuse light for at least 1 day. The absorbance is a linear function of concentration, at least up to 1·0 μg of cadmium per ml. The absorbance of 12·1 μg of cadmium per 20 ml of chloroform-dithizone solution is approximately 0·44 when 1-cm cells are used. Inasmuch as the Lambert (Bougher) Law is obeyed, a similar absorbance is obtained from 2·42 μg of cadmium when 5-cm cells are used.

Effect of other elements

In testing the effect of other elements on the determination of cadmium by the procedure described, the elements were added to solutions containing the appropriate amounts of beryllium sulphate, sulphuric and hydrochloric acids before the precipitation with benzotriazole.

No interference was caused by the presence of 10-mg amounts of Al, Sb^{III}, As^{III}, Ba, Bi, B, Br, Ca, Ce^{IV}, Cs, Cr^{III}, Co, Cu^{II}, Dy, Er, Eu, F, Gd, Ga, Ge, Au, Hf, Ho, In, I, Ir, Fe^{III}, La, Pb, Li, Lu, Mg, Mn^{II}, Hg^{II}, Mo^{VI}, Nd, Ni, Nb, Pd^{IV}, P(as PO_4^{3-}), Pt^{IV}, K, Pr, Re, Rh, Rb, Sm, Sc, Se^{IV}, Si, Na, Sr, Ta, Te^{IV}, Tb, Tl^{I}, Th, Tm, Sn^{II}, Ti^{III}, W^{VI}, U^{VI}, V^{V}, Yb, Y, or Zr or 100 μg of zinc. The interference of larger amounts of zinc may be eliminated as described later.

It should be noted that the preliminary precipitation with benzotriazole separates cadmium from all but the following elements: zinc, cobalt, copper, nickel and silver (if present, silver should be removed as silver chloride). The subsequent anion-exchange step provides a solution containing only cadmium and zinc.

If the preliminary benzotriazole precipitation step is omitted and chloride solutions of the sample containing 10 mg of the above listed elements are passed directly through the anion-exchange columns, results are within the stated accuracy limits with the following limitations:

(1) Thallium is adsorbed by the resin in a chloride medium and will strongly interfere with the final cadmium determination unless additional remedial steps are taken.

(2) Mercury is also adsorbed by the resin and is only incompletely removed by evaporating the sulphuric acid solution to dryness.

(3) Platinum, palladium, iridium and rhodium are retained by the resin. They largely remain on the column when the cadmium is eluted, and tend to make the columns useless for further analytical purposes.

(4) Gold is also retained by the resin and its removal is difficult.

(5) Lead quantitatively accompanies the cadmium. Its interference is almost identical to that described for zinc and can be obviated in the same manner.

Effect of zinc

If more than 100 μg of zinc are present in the aliquot, some of the dithizone is consumed to convert a small portion of the zinc in the aqueous layer to a dithizone compound. The aqueous layer is then coloured red (depending, of course, on the amount of zinc present) and more dithizone is needed to extract the cadmium. The presence of zinc in interfering amounts may be ascertained by making a second dithizone extraction of the aqueous phase. A pink colour indicates either zinc or cadmium. In this case proceed as follows:

Extract twice with 20 ml of dithizone solution, combining the extracts in another separatory funnel. Revert the cadmium by extracting the chloroform phase with 20 ml of 6M sulphuric acid. Evaporate the aqueous phase to dryness, dissolve the salts, and extract the cadmium as described in the procedure. The interference of up to 10 mg of zinc may be eliminated in this manner. An alternative method of separating cadmium and zinc, which has been successfully used for the determination of cadmium in 1-g samples of zinc, is by a cation-exchange separation from 0·3M hydriodic acid —0·075M sulphuric acid. Cadmium forms an iodide complex which is not retained on a cation resin whereas zinc is adsorbed.[5]

APPLICATION OF THE METHOD

A sample of beryllium oxide analysed for cadmium using this procedure was found to contain less than 0·1 ppm of cadmium. The recovery of cadmium added to this sample of beryllium oxide is shown in Table II.

TABLE II. RECOVERY OF CADMIUM ADDED TO BERYLLIUM OXIDE

BeO, *g*	Cd added, μg	Cd found μg
1	3·0	3·3[a]
1	8·0	7·6
3	1·0	1·2[a]
5	0·5	0·25[a]
1	10·0	10·4
1	25·0	23·8
1	50·0	51·9
1	100·0	97·3
2	100·0	103·5

[a] 5-cm cells used. 1-cm cells used for other determinations.

Blank values corresponding to 0·02 μg of cadmium were obtained with the amounts of reagents used during the analysis.

Results obtained when the method was applied to New Brunswick Laboratory standard samples of beryllium oxide are shown in Table III.

TABLE III. ANALYSIS OF NBL STANDARDS

Sample[a]		Cd found, μg	Nominal Value
Be	85	0·41, 0·47	
	86	0·48, 0·46	
	87	0·47, 0·47	
	88	0·40, 0·44	
BeO	72-1	2·1, 2·2, 2·1[b]	2·16
	72-2	1·2, 1·2	0·72[c]
	72-3	0·8, 0·8	0·36[c]
	72-4	0·7, 0·7	0·18[c]
	72-5	0·45, 0·50	?

[a] 2-g samples were taken for the above determinations. 5-cm cells were used for absorbance measurements.

[b] The results in this table were obtained at Ledoux. Sample 72-1, analysed at General Electric Company was found to contain 1·9, 2·0, and 2·0 ppm of cadmium.

[c] Based upon amount added to 72·5.

Zusammenfassung—Eine Methode zur Bestimmung von Cadmium in Beryllium und Berylliumoxyd wird beschrieben. Unter Verwendung von Nickel als Träger wird Cadmium mit Benzotriazol gefällt. Zur Abtrennung weiterer Metalle wird die chloridlösung durch einen Anionenaustauscher (Dowex-1) Die Methode ist auf ±3% oder 0·3 μg genau, was immer grösser ist. Keine Störungen werden verursacht durch Anwesenheit von 10-mg Mengen von 68 anderen Elementen.

Résumé—Les auteurs décrivent une méthode de dosage du cadmium dans le beryllium ou l'oxyde de beryllium. Le cadmium est précipité par du benzotriazole en utilisant du nickel comme entraîneur. Une séparation ultérieure des autres éléments est faite en faisant passer une solution de chlorure sur une résine Dowex 1 échangeuse d'anions. Le cadmium est dosé finalement par la dithizone. La précision de la méthode est ±3 pour cent ou 0,3 μg de cadmium. La présence de 68 éléments en quantité de 10 mg ne gêne pas le dosage.

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TETRACYANOETHYLENE CHEMISTRY

INDIRECT PHOTOMETRIC DETERMINATION OF ANTHRACENE IN NAPHTHALENE

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Summary—Anthracene can be determined in naphthalene indirectly by measuring the destruction of the colour of a naphthalene-tetracyanoethylene (TCNE) complex after anthracene and TCNE have reacted via the Diels-Alder reaction. A trace analysis method of indirect spectrophotometry can be used to extend the determination to as low as 0·01% (5×10^{-5} *M*) of anthracene in the final solution in a ten thousand-fold excess of naphthalene. Pentamethylbenzene can be used instead of naphthalene but it is a less desirable reagent. Various possible interferences have been studied.

INTRODUCTION

UNTIL recently there were available few simple colorimetric methods for detection or determination of anthracene or other aromatic hydrocarbons. Novel methods have been developed for the detection of anthracene and other hydrocarbons using piperonal chloride and benzal chloride,[1,2] isatin,[3] and 3-nitro-4-dimethylaminobenzaldehyde.[4]

In addition, ultraviolet spectrophotometry following chromatographic separation on alumina[5] has been applied to the determination of anthracene and other polynuclear aromatic hydrocarbons. Anthracene has also been determined fluorimetrically.[6]

Apparently no colorimetric methods have utilised the Diels-Alder reaction of anthracene. Extensive studies of tetracyanoethylene (TCNE) and its coloured complexes with aromatic hydrocarbons[7] suggested a simple indirect colorimetric method for anthracene. Advantage was taken of the rapid and quantitative Diels-Alder reaction of TCNE with anthracene at room temperature[8] in contrast to maleic anhydride which reacts rapidly at reflux temperature with anthracene,[9] but only slowly at room temperature.[10]

The pertinent data on the coloured π-complexes of TCNE, as summarised in Table I, suggested a colorimetric measurement of anthracene based on the destruction of the colour of a complex of TCNE and excess naphthalene:

$$\underset{\text{(red complex)}}{C_{10}H_8(\text{TCNE})} + C_{14}H_{10} \rightarrow C_{10}H_8 + \underset{\text{(colourless adduct)}}{C_{14}H_{10}\text{—TCNE}}$$

These coloured complexes have been utilised in paper chromatography.[11]

Naphthalene was selected to form the coloured complex since it is frequently found in large amounts in mixtures of aromatic compounds, is quite soluble in chloroform,

TABLE I.—π-COMPLEXES OF TCNE AND AROMATIC HYDROCARBONS

Aromatic Hydrocarbon	K	λ_{max}, mμ	ε
Cyclohexene	0·247	422	4760
Benzene	2·0	384	3570
Toluene	3·7	406	3330
Naphthalene	11·7	550	1240*
Pyridine	12·0	421	10500*
Fluorene	18·0	570	1430*
Pyrene	29·5	724	1137*
Pentamethylbenzene	123·0	520	3270

* Second absorption maximum omitted

does not complex the TCNE too strongly, and has an absorption maximum well removed from the 400-mμ region in which some aromatics absorb strongly.

EXPERIMENTAL

Reagents

Tetracyanoethylene (TCNE) was kindly supplied by the Central Research Department, Experimental Station, E. I. duPont de Nemours and Company, or was synthesised.[12] It was purified to a white powder by sublimation.

Anthracene was recrystallised four times from diethyl ether. Sublimed naphthalene, pentamethylbenzene, and other materials were used as received. Cyclopentadiene was prepared by cracking dicyclopentadiene at 160° and taking the middle fraction of cyclopentadiene distilling at 40°.

Chloroform and methylene chloride were of reagent grade.

TCNE reagent, naphthalene, 0·75M trace analysis solution: Dissolve 12·8 mg of TCNE in 15 ml of methylene chloride and add 9·6 g of naphthalene. Dilute with 50 ml of chloroform prior to the addition of the sample. For the pure chromogenic reagent, dilute to exactly 100 ml with chloroform; this reagent had an absorbance of about 0·9 on the Bausch and Lomb Spectronic 20 Colorimeter.

TCNE reagent, naphthalene, 0·05–0·50M solutions: Dissolve 51·2 mg of TCNE in 15 ml of methylene chloride, or in 1 ml of triethyl phosphate or dimethoxyethane. Add 0·64 to 6·4 g of naphthalene for the desired molarity. Dilute with 50 ml of chloroform before the addition of the sample. See Table IV for the stability of 0·25M naphthalene reagent.

TCNE reagent, pentamethylbenzene, 0·10M: Prepare as above using 5·1 mg of TCNE and 1·48 g of pentamethylbenzene instead of naphthalene.

Procedures

(*a*) Anthracene, 0·5–5 × $10^{-4}M$ (final solution): Add a 10- or 25-ml aliquot, containing 0·9 to 9 mg of anthracene in chloroform or alkane solvent, to the 0·75M naphthalene trace analysis reagent; dilute to exactly 100 ml with chloroform. After 40 min at room temperature, measure at 550 mμ according to Method C.[13] Set the instrument to read 0% transmission in the darkness and 100% transmission with the *sample solution* in the light path, then read the % transmission or absorbance with the pure chromogenic reagent in the light path. The last two operations obviously must be performed for each sample and for each point on a calibration curve covering the 0·5 to 5 × $10^{-4}M$ anthracene concentration range (see Fig. 2).

(*b*) Anthracene, 0·3–3·9 × $10^{-3}M$ (final solution): Add a 10- or 25-ml aliquot, containing 5·3 to 70 mg of anthracene in chloroform or alkane solvent, to the 0·05M naphthalene reagent; dilute to exactly 100 ml with chloroform. After 40 min at room temperature, measure at 550 mμ. Prepare a calibration curve for this range as shown in Fig. 1.

If naphthalene is present in the sample, add only sufficient naphthalene to the reagent to bring the final concentration to 0·05M. If no interferences are present, mix the sample and TCNE before adding naphthalene, to reduce the reaction time.

Anthracene in the 1·5 to 3·5 × $10^{-4}M$ range in the final solution may be determined similarly using 0·1M pentamethylbenzene reagent, a reaction time of 2 to 4 hr, and a wavelength of 520 mμ.

(*c*) Anthracene in cyclopentadiene: Add an excess of maleic anhydride of no more than 0·4 g to the sample at room temperature and allow it to react with the cyclopentadiene for 2 to 3 hr. The presence of the yellow maleic anhydride-anthracene complex[14] after that time indicates that excess anhydride is present. Follow procedures (*a*) or (*b*) for the determination of anthracene.

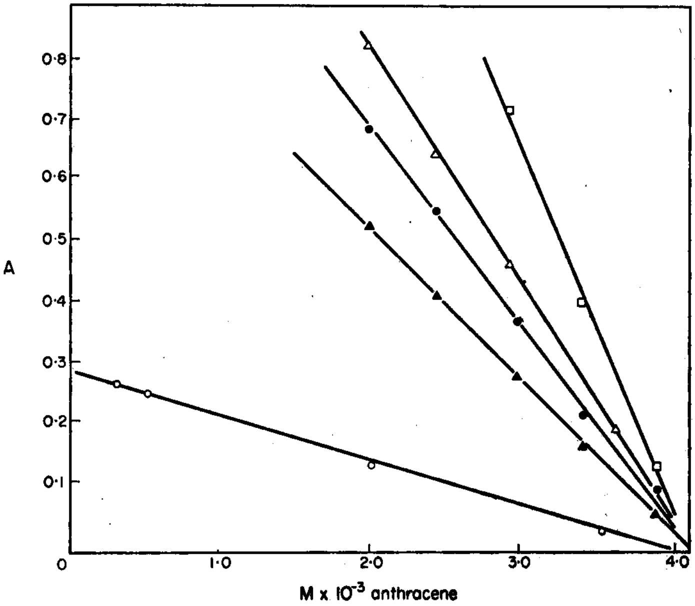

FIG. 1.—Initial TCNE 4 × $10^{-3}M$
Naphthalene: 0·05M ○
0·15M ▲
0·20M ●
0·25M △
0·50M □

DISCUSSION OF RESULTS

Fig. 1 shows various calibration curves of absorbance versus concentration of anthracene using naphthalene–TCNE reagents. These curves show conformity to Beer's Law up to about 3·9 × $10^{-3}M$ anthracene. The absorbance is not zero when the stoichiometric amount of anthracene has been added to the TCNE. The anthracene may not have been 100% pure or it may be that the equilibrium is not favourable in this concentration range.[13] The last traces of TCNE are complexed by a proportionately large concentration of naphthalene. Although the 0·05M naphthalene reagent gives a satisfactory range in procedure (*b*), 0·10 or 0·15M reagents may be used for greater sensitivity and only a slightly smaller range.

One advantage of using naphthalene is that its relatively small stability constant (see Table 1) permits a variation in the concentration of naphthalene, and a concomitant variation in the sensitivity of the method, without retarding the Diels-Alder reaction appreciably. A second advantage is, that if a large amount of naphthalene is present with the anthracene, it can be used to form the coloured complex. Thus, in general, a large amount of an interfering aromatic hydrocarbon need not be an interference, but it can be used to form the coloured aromatic–TCNE complex for the analysis. This method serves as a model system for the determination of other Diels–Alder aromatic dienes.

Unfortunately, at high concentrations of naphthalene, concentrations of anthracene below 3 × $10^{-3}M$ cannot be measured without resorting to the trace analysis method described below. Also, the actual molar absorptivity as shown in Table 1 is not approached, it being 58 for 0·05*M* and 540 for 0·50*M* naphthalene.

To make analytical use of the favourable slope of the calibration curve for 0·75*M* naphthalene, trace analysis Method C[13] is used to extend the analysis to the $10^{-5}M$ range. This method yields a plot in which absorbance increases with increasing concentration of anthracene as shown in Fig. 2.

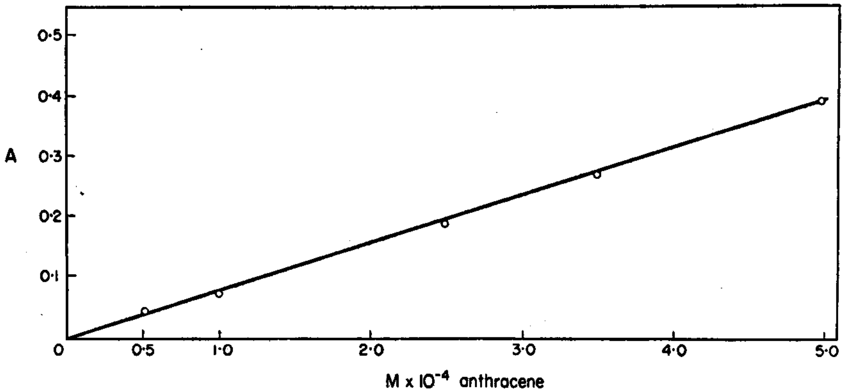

FIG. 2.—Naphthalene 0·75*M*: Initial TCNE 1 × $10^{-3}M$

In this method, the extremely sensitive 0·75*M* naphthalene reagent is used to obtain readings at the more accurately read section of the absorbance scale. In ordinary indirect methods, a low concentration of anthracene would give high absorbance readings, which are less accurately read.

TABLE II.—DETERMINATION OF ANTHRACENE

Procedure	Interference	Anthracene	
		Present, *mg*	Found, *mg*
(*a*)	None	0·91	1·07
(*a*)	None	1·82	1·71
(*b*)	0·23*M* benzene	36·4	34·5
(*b*)	0·23*M* benzene	52·8	53·5
(*b*)	0·188*M* toluene	52·8	54·0
(*b*)	0·188*M* toluene	71·0	71·0

Thus, this is the recommended method for determining small amounts of anthracene. It compares favourably with the sensitivity of the ultraviolet absorption bands of anthracene in the 375-mμ region.

Table II contains results obtained in the determination of anthracene by both procedure (*a*) and procedure (*b*).

Using the pentamethylbenzene reagent lowers the range of the analysis to $10^{-4}M$ since pentamethylbenzene forms a complex ten times stronger than naphthalene, as shown in Table I. One disadvantage is that the calibration curve fails to follow Beer's Law at concentrations of anthracene approaching the stoichiometric point. In addition, the absorbance is not constant until after a reaction time of 2 to 4 hr, as shown in Table II. These factors make it undesirable to increase the concentration of pentamethylbenzene to match the sensitivity of the 0·50 to 0·75M naphthalene curves. Hence this reagent is not recommended where the naphthalene reagent can be used.

TABLE III.—TIME STUDY OF 4 × $10^{-4}M$ TCNE-0·1M PENTAMETHYLBENZENE AT VARIOUS ANTHRACENE CONCENTRATIONS

Time, *hr*	% Transmittance			
	2·0	2·9 (× $10^{-4}M$) anthracene	3·4	3·9
1	45	63	70	75
2	47	68·5	80	81·5
4	47	71	85	86
4 days	47	75	93	92

The results in Table IV demonstrate the stability of the naphthalene–TCNE complex after reaction with varying amounts of anthracene. This appears to rule out appreciable alkylation of naphthalene at room temperature similar to the alkylation of phenanthrene.[15]

TABLE IV.—STUDY OF STABILITY OF TCNE COMPLEXES

Time	4 × $10^{-3}M$ TCNE, 0·25M naphthalene			2 × $10^{-3}M$ TCNE, 0·0125M pentamethylbenzene, 1·95 × $10^{-3}M$ anthracene
	2·0	2·9 (× $10^{-3}M$) anthracene	3·9	
40 min	14·5%	36·5%	85·0%	88·5%
1 month	14·0	37·0	86·0	89·5
4 months				89·5
5 months	14·0	37·5	87·0	
6 months*				93·0
7 months*	14·0	37·0	79·0	

* Taken out of hood and left in sunlight

The constant absorbance of such solutions after 5 to 7 months indicates that the complex may be prepared in advance and used when desired. The change in absorbance of one of the solutions from the 5th month to the 7th month may possibly be attributed to putting the solutions in the sunlight. It is recommended to store the reagents in a cool dark place such as a hood.

Such a constant absorbance also demonstrates that the Diels-Alder reaction is essentially complete and that there is no measurable reverse Diels-Alder reaction taking place.

INTERFERENCES

Table V summarises the interference tested on the TCNE-naphthalene complex. The possible interferences are alkenes, aromatic or alkyl dienes, substituted benzenes, polynuclear aromatic hydrocarbons, phenols, amines, alcohols, water, and thiols.

In general, it can be predicted from Table 1 that substances with a small stability constant relative to naphthalene will not interfere and *vice versa.* Thus, large amounts of alkenes like cyclohexane should not interfere. Likewise, large amounts of benzene and toluene should not interfere, and this is verified in Table V. In contrast, even small amounts of pentamethylbenzene interfere.

TABLE V.—INTERFERENCES: $4 \times 10^{-3}M$ TCNE, $0{\cdot}25M$ NAPHTHALENE, $2{\cdot}9 \times 10^{-3}M$ ANTHRACENE (IN 1 hr), PROCEDURE (*b*)

Interference	*M*	% Transmittance
None	—	36·5%
Benzene	0·46	38·0
Toluene	0·188	35·5
Indene	50×10^{-3}	30·5
Phenanthrene	30×10^{-3}	31·5
Chrysene	30×10^{-3}	34·5
Fluoranthene	10×10^{-3}	32·0
Pyridine	6×10^{-3}	66·0
β-Naphthol	30×10^{-3}	31·5
α-Naphthol	10×10^{-3}	41·5
Anthraquinone	0·01 No interference if used as blank	
Cyclopentadiene	0·016	35·0 (Maleic anhydride added)

The interference of a number of polynuclear aromatic hydrocarbons at the 0·01*M* level is minimal, with fluoranthene being an exception. Indene, which apparently reacts somewhat with TCNE at the macro level, does not interfere in 1 hr at this level to any greater degree than phenanthrene.

Phenols and aromatic hydrocarbons with an activated position, such as phenanthrene, are C-alkylated by TCNE at room temperature.[15] However, low yields are obtained with phenols unless a catalyst such as pyridine is used.[15] Complexing TCNE with naphthalene apparently slows alkylation of β-naphthol as well as phenanthrene since they do not interfere seriously, as shown in Table V.

Diels-Alder active dienes will interfere since they will react as anthracene. The interference of highly reactive dienes, such as cyclopentadiene, can be minimised by first adding sufficient maleic anhydride to react with the cyclopentadiene, as shown in Table V. Maleic anhydride reacts only very slowly with anthracene at room temperatures.[10] Ammonia, hydrazine, and primary and secondary amines react rapidly with TCNE, releasing hydrogen cyanide. Even a small amount of aniline destroys the red colour of a naphthalene–TCNE complex. Small amounts of pyridine interfere seriously, as shown in Table V.

Alcohols apparently do not react with TCNE without a catalyst such as urea or zinc acetate. Water hydrolyses TCNE slowly, and thiols reduce it.[8]

The effect of heating TCNE-aromatic complexes has been reported to destroy the colour.[16]

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Zusammenfassung—Mengen von bloss 0·5% Anthrazen können in Naphthalin indirekt bestimmt werden. Man misst das Ausbleichen der Farbe des Naphthalin-Tetracyanoathylen (TCÄ)-Komplexes, nachdem Anthracen und TCÄ eine Diels-Alder Reaktion eingegangen sind. Eine Methode für Spurenanalyse basiert auf einer indirekten photometrischen Bestimmung nach diesem Verfahren und dehnt den Mengenbereich herunter zu 0·01% Anthracen in Naphthalin. Pentamethylbenzol kann an Stelle von Naphthalin verwendet werden, aber ist ein weniger gutes Reagens. Eine Anzahl möglicher Störungen wurde studiert.

Résumé—Une quantité aussi faible que 0,5 pour cent d'anthrécène dans le naphtalène peut être dosée indirectement par la mesure de la destruction de la couleur d'un complexe naphtalène-tétracyanoéthylène (TCNE), l'anthracène et le TCNE réagissant au moyen de la réaction de Diels-Alder. Une méthode spectrophotométrique indirecte d'analyse de trace peut être utilisée pour étendre le dosage jusqu'à une quantité aussi faible que 0,01 pour cent d'anthrécène dans le naphtalène. Le pentaméthylbenzène peut être autilisé à la place du naphtalène, mais c'est un réactif moins désirable. Un certain nombre d'interférences possibles ont été étudiées.

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THE FLAME PHOTOMETRIC DETERMINATION OF TRACES OF SODIUM AND POTASSIUM IN THE PRESENCE OF OTHER METALS, AND METHODS FOR OVERCOMING SOME INTERFERENCES

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Summary—A study has been made of the interferences caused by the major metals in the flame photometric determination of sodium and potassium in inorganic salts using an EEL flame photometer. Many metals do not interfere, enabling a straightforward determination to be made. Methods of overcoming the interference of certain other metals include suppression of their flame emissions with aluminium nitrate or their removal by ion-exchange methods before the determination of sodium and potassium.

INTRODUCTION

FLAME photometry provides the simplest method for the determination of small amounts of sodium and potassium, and the Evans Electroselenium Ltd. (EEL) flame photometer[1] is one of the instruments widely employed for this purpose. However, when this instrument is used for the determination of alkali impurities in inorganic salts, in some cases the major metal itself emits radiation which is not completely absorbed by the filters used.

A comprehensive investigation of interference has been carried out for the Perkin Elmer Model 18 instrument,[2] but work with the EEL instrument has been confined to a study of mutual interferences of the alkali metals,[3,4] calcium[5] and some anions.[1]

It was decided to carry out a survey of a fairly wide range of inorganic salts using an EEL instrument in order to discover those metals which cause interferences, and to provide methods for overcoming the difficulty, wherever possible.

EXPERIMENTAL

Apparatus

A standard EEL (Evans Electroselenium Ltd.) flame photometer was used for this work. This instrument, together with its associated filters, has been described by Collins and Polkinhorne.[1]

The preparation of purified solutions of metals and the examination of flame photometric interferences

Purified solutions of the metals were prepared using chemical separation to remove alkali metals when they were known to be present. The methods used are summarised in the Appendix.

The EEL flame photometer was zeroed at full sensitivity against an appropriate blank solution prepared from quantities of reagents similar to those used to prepare the metal solution. Each metal solution was then examined in the EEL flame photometer, and the galvanometer deflection was noted when the sodium and potassium filters were used in turn. Appreciable galvanometer deflections were obtained in many cases (see Table I). In some cases, the transmitted emission was so great that the solution had to be diluted in order to obtain a galvanometer deflection falling within the scale. In such cases the observed deflection was multiplied by the dilution factor. These results were checked by using a different purification procedure and hence it was assumed that the deflections produced were due to emissions from the major metal and not to traces of alkali metals.

TABLE I.—GALVANOMETER DEFLECTIONS FOR INTERFERING METALS

Metal	Method of purification* (see Appendix)	Galvanometer deflection†	
		Sodium filter	Potassium filter
Ba	(a)	71	1200
	(b)	82	1200
Ca	Known to interfere; not examined		
Ce	—	64	69
Cr	(a)	164	220
	(b)	168	152
Co	(a)	59	72
	(b)	58	67
Cu	(a)	22	2
	(b)	29	2
Fe	(a)	140	184
	(b)	136	87
Mn	(a)	56	46
	(b)	56	48
Ni	(a)	62	96
	(b)	78	106
Sr	Known to interfere; not examined		
U	(a)	38	53
	(b)	32	24
	(c)	46	28

* A concentration of 1 g/100 ml was used.

† Full scale deflection (100 units) was given by 2·3 μg/ml of sodium or 3·1 μg/ml of potassium.

All other metals examined gave no significant deflection, and it should therefore be possible to determine sodium and potassium in solutions of these metals by a direct method. To prove this conclusively the recovery of known additions of sodium and potassium from aqueous solutions of commercial salts of these metals was determined. The results obtained are given in Table II.

Throughout this work the addition method of estimating the results was used.[6] This method is simple and is less likely to be affected by interfering elements than other methods, but it is not strictly accurate for sodium as the galvanometer response/concentration curve for this element is not quite linear. The results obtained, however, are sufficiently accurate for normal routine purposes. The results throughout this paper are reported to the nearest 5 ppm.

Except for tungsten, for which erratic results were observed, satisfactory recoveries of sodium and potassium were obtained, especially when it is considered that the percentage recovery was often calculated with reference to high blank values.

It was concluded that sodium and potassium may be directly determined as impurities in solutions of the following metals: aluminium, beryllium, bismuth, cadmium, lead, magnesium, molybdenum, tin, silver, and zinc. Furthermore, it was established that these metals do not affect the approximate linearity of the galvanometer response/concentration curve for sodium and potassium.

Sodium and potassium cannot be directly determined in the presence of those elements which produce interfering flame emissions unless the blank solution contains an equivalent amount of the pure metal. This procedure would not be very satisfactory since, in most cases, it would not be possible to zero the instrument, and this would result in a considerable loss in the working area of the galvanometer scale.

The suppression of interferences with aluminium nitrate

Aluminium nitrate suppresses the flame emissions of calcium[7-9] and strontium.[7,9,10] This has been used to prevent interference from strontium[11] and calcium[8,12] in the determination of sodium.

TABLE II.—RECOVERIES OF SODIUM AND POTASSIUM BY DIRECT FLAME PHOTOMETRY

Metal	Compound used	Metal concentration, % *w/v*	Sodium			Potassium		
			Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %
Al	Aluminium sulphate	1·0	0	140		0	70	125
			200	340	100	200	320	
Be	Beryllium sulphate	0·05	0	10		0	0	80
			200	240	115	200	160	
Bi	Bismuth nitrate	1·0	0	30		0	10	90
			200	250	110	200	190	
Cd	Cadmium chloride	1·0	0	40		0	10	105
			200	260	110	200	220	
Pb	Lead acetate	1·0	0	10		0	0	110
			200	200	95	200	220	
Mg	Magnesium chloride	0·12	0	10		0	20	95
			200	240	115	200	210	
Mo	Ammonium molybdate	0·08	0	130		0	310	100
			200	370	120	200	510	
Sn	Tin^{II} chloride	1·0	0	150		0	10	90
			200	390	120	200	190	
Ag	Silver nitrate	1·0	0	30		0	10	105
			200	240	105	200	220	
W	Ammonium tungstate	1·0	0	60		0	100	30
			200	360	150	200	160	
			0	50		0	180	70
			200	420	185	200	320	
Zn	Zinc sulphate	1·0	0	50		0	10	100
			200	280	115	200	210	

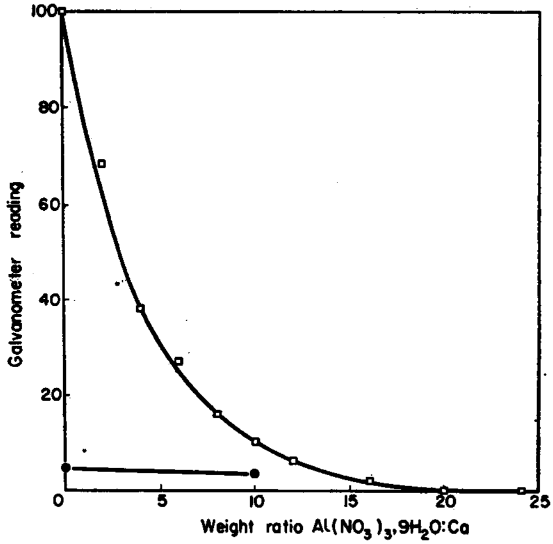

FIG. 1.—The effect of aluminium nitrate on the flame emission of calcium.
□ Na filter
● K filter

It was decided to investigate the influence of aluminium nitrate on the flame emissions of calcium, strontium, barium and cerium in the determination of sodium and potassium.

Calcium. A series of test solutions was prepared consisting of 1% w/v calcium chloride solution and varying proportions of aluminium nitrate. Each test solution was examined at full sensitivity by the flame photometer, and the scale readings were noted when the sodium and potassium filters were used in turn. The results obtained are given in Fig. 1.

From these results it was concluded that the potassium filter effectively absorbs most of the unwanted emission but that a 20 : 1 weight ratio of aluminium nitrate is required to suppress the calcium emission which passes through the sodium filter.

Known amounts of sodium and potassium were added to a 1% w/v solution of calcium chloride, aluminium nitrate nonahydrate was added in the ratio of 25 : 1 with respect to calcium, and the sodium and potassium were determined flame photometrically, employing the addition technique. The results obtained are given in Table III and show that satisfactory recoveries are possible.

Strontium. Jones[11] has shown that aluminium nitrate may be used to suppress the strontium emission in the determination of sodium.

Tests showed that the strontium emission passing through the potassium filter can be effectively suppressed by adding aluminium nitrate nonahydrate in the weight ratio of 25 : 1 with respect to strontium.

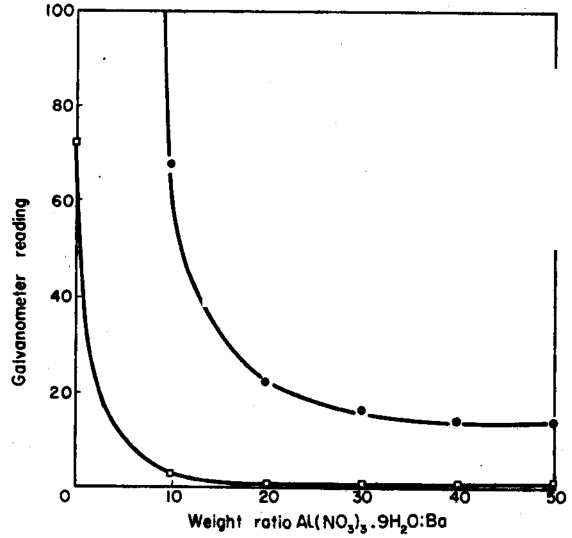

FIG. 2.—The effect of aluminium nitrate on the flame emission of barium.
□ Na filter
● K filter

TABLE III.—DETERMINATION OF KNOWN CONCENTRATIONS OF SODIUM AND POTASSIUM IN CALCIUM CHLORIDE, WITH ALUMINIUM NITRATE NONAHYDRATE PRESENT IN THE WEIGHT RATIO OF 25 : 1 WITH RESPECT TO CALCIUM

Sodium			Potassium		
Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %
0	10	—	0	15	—
50	60	100	100	120	105
100	110	100	200	220	105
150	160	100	300	330	105

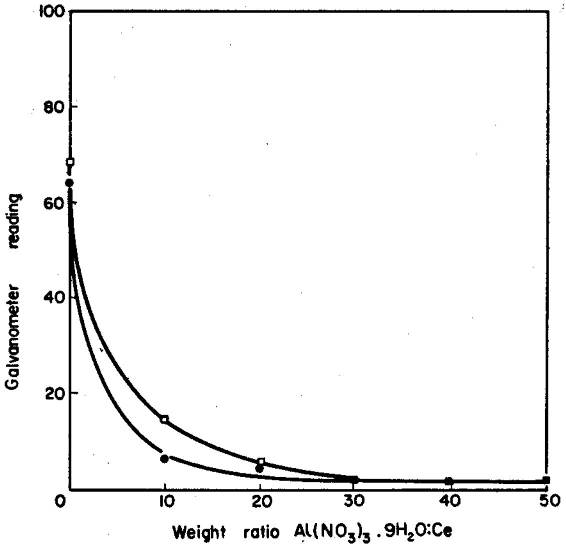

FIG. 3.—The effect of aluminium nitrate on the flame emission of cerium.
□ Na filter
● K filter

Barium and Cerium. Purified 1% aqueous solutions of barium and cerium were prepared as in the Appendix, method (*a*) being used for barium.

Varying proportions of aluminium nitrate were added to the barium and cerium solutions, and these were run through the flame photometer at full sensitivity, after the instrument had been zeroed in each case against a blank solution containing a similar concentration of aluminium nitrate. The galvanometer deflections obtained are given in Figs. 2 and 3.

The results showed that the flame emission of cerium which normally passes through the sodium and potassium filters may be almost completely suppressed by a thirty-fold weight of aluminium nitrate nonahydrate.

A similar proportion of aluminium nitrate also successfully suppressed the barium flame emission passing through the sodium filter. The results obtained for barium and the potassium filter were inconclusive and a further check was made, using 1% barium solutions prepared directly from AnalaR barium chloride, and from barium chloride followed by single and double precipitations with ammonium carbonate.

Employing a 45% concentration of aluminium nitrate and the potassium filter a galvanometer deflection of about 16 units was obtained in each case. It was concluded that it is not possible to suppress completely that part of the barium flame emission which passes through the potassium filter.

The recovery of known additions of sodium and potassium from ammonium cerium^{IV} nitrate

Using a 1% w/v solution of ammonium cerium^{IV} nitrate to which known additions of sodium and potassium had been made, it was found possible to obtain good recoveries after the addition of 10% w/v hydrated aluminium nitrate. The results are shown in Table IV.

The effect of aluminium nitrate on the flame emissions of certain other metals

Aluminium nitrate was found to be ineffective in the suppression of unwanted radiation in the case of the following metals: chromium, manganese, iron, uranium, nickel, cobalt, and copper.

The removal of some interfering metal ions by ion-exchange methods

Ion-exchange techniques are now widely used for removing interfering ions in various analytical methods and it seemed likely that some of these techniques could be used for the removal of interfering ions before the flame photometric determination of sodium and potassium.

Copper was not investigated as it can be readily removed by electrolysis.

TABLE IV.—RECOVERY OF SODIUM AND POTASSIUM FROM AMMONIUM CERIUM^{IV} NITRATE

Sodium			Potassium		
Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %
0	140	—	0	15	—
0	150	—	0	5	—
0	150	—	0	5	—
50	210	120	50	65	110
100	265	115	100	120	110

Chromium^{VI} and Manganese^{VII}. Preliminary tests showed that 0·5 g of chromium, as potassium dichromate, was readily absorbed on a 1- × 20-cm column of Amberlite IRA-400(Cl) resin.

On this basis, the following procedure was tried:

A 1- × 20-cm column of Amberlite IRA-400(Cl) was prepared and washed well with water. The sample solution, containing 0·5 g of the chromium^{VI} and known additions of sodium and potassium dissolved in about 10 ml of water, was allowed to pass down the column at the rate of about 1 drop/sec. One hundred ml of water were then passed down the column at about 2 drops/sec. The combined eluate was reduced to a volume of 50 ml by evaporation and dilution to volume in a graduated flask, and sodium and potassium were determined in the usual way.

A similar procedure was used for manganese^{VII} in the form of potassium permanganate, with the exception that the sample was dissolved in 25 ml of water, instead of in 10 ml, and the solution was passed through the column at a rate of 2 drops/sec.

The recoveries of sodium and potassium obtained are shown in Table V. The apparent sodium and potassium contents found without separation are also listed.

TABLE V.—RECOVERIES OF SODIUM AND POTASSIUM FROM POTASSIUM PERMANGANATE, POTASSIUM DICHROMATE AND CHROMIUM TRIOXIDE, USING AN IRA-400 (Cl) COLUMN FOR REMOVAL OF THE INTERFERING ION

Compound	Proposed Method						Without Separation	
	Sodium			Potassium			Sodium	Potassium
	Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %	Found, *ppm*	Found, *ppm*
Potassium permanganate (4 samples)	0	95	—	—	—	—	210	—
	200	300	105					
	0	75	—					
	200	290	110					
	0	120	—					
	200	320	100					
	0	100	—					
	200	320	110					
Potassium dichromate	0	510	—	—	—	—	1100	—
	200	700	95					
Chromium trioxide (2 samples)	0	205	—	0	40	—	615	550
	200	435	115	200	240	100		
	0	220	—	0	30	—		
	200	460	120	200	210	90		

The results showed that this technique effectively removed manganese^{VII}, and chromium^{VI} and good recoveries of sodium and potassium were obtained.

Uranium. In sulphuric acid solution, uranium forms a complex anion, $[UO_2(SO_4)_n]^{2-2n}$, which may be absorbed by quaternary anion-exchange resins and this fact has been widely used as a technique for separating uranium from other elements.[14–18]

A column of Amberlite IRA-400 in the sulphate form was prepared and it was found that absorption of the uranium was complete from solutions 0·1*N* with respect to sulphuric acid.

The sample, containing about 0·5 g of uranium and known additions of sodium and potassium, was dissolved in 10 ml of 0·1*N* sulphuric acid and the solution was passed down a 1 × 30-cm column of Amberlite IRA-400(SO_4). The column was allowed to run at a rate of 1 drop/sec. The column was washed with 100 ml of 0·1*N* sulphuric acid, and the combined eluate was reduced to a volume of 50 ml by evaporation and adjustment in a graduated flask. The sodium and potassium were then determined in the usual way. The compounds used were AnalaR uranyl nitrate and AnalaR uranyl acetate, and the results obtained are given in Table VI.

TABLE VI.—RECOVERIES OF SODIUM AND POTASSIUM FROM URANIUM SALTS, USING AN IRA-400(SO_4) COLUMN FOR REMOVAL OF THE URANIUM

Compound	Sodium			Potassium		
	Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %
Uranyl nitrate	0	80	—	0	25	—
	200	280	100	200	210	95
Uranyl acetate	0	100	—	0	20	—
	200	305	105	200	230	105

The results showed that the uranium had been effectively removed from the solution, and good recoveries of sodium and potassium were obtained.

Manganese^{II}, Nickel, Cobalt, Chromium^{III} and Iron. Samuelson *et al.*[19,20] have developed a method for separating alkali metals from many other metals when both constituents are present in approximately equal amounts. They passed the solution down a column of a strong anion-exchange resin (Dowex 2) in the EDTA-form. The interfering metal was held by the resin as its EDTA complex while the alkali metals passed through in the eluate.

It was decided to apply this technique to the separation of traces of alkali metal impurities from the interfering metals.

Amberlite IRA-400(Cl) was used, this being an equivalent of Dowex 2. Samuelson *et al.*[19] converted the resin to the EDTA form by successive treatments with sodium acetate and disodium ethylenediaminetetra-acetate. For this work, ammonium salts were used to avoid contaminating the resin with sodium.

The resin column was prepared as follows:

A slurry of Amberlite IRA-400(Cl) was tipped into a 1-cm diameter glass column to a height of about 60 cm. Two hundred ml of 10% w/v ammonium acetate solution was passed through the column at a rate of 1 drop/sec. The column was then washed with 100 ml of water.

Ten g of ethylenediaminetetra-acetic acid was suspended in 100 ml of water and ammonium hydroxide solution (sp. gr. 0·880) was added until the free acid had dissolved. The filtered solution was allowed to percolate through the column at a rate of 1 drop/sec. Finally the column was washed with 500 ml of water.

This procedure was also found to be suitable for the regeneration of a column loaded with nickel, cobalt or manganese. Chromium was tenaciously held by the column and 600 ml of 10% w/v ammonium acetate solution was necessary to remove it. Iron^{III} was best removed by ammonium acetate solution which had been half-saturated with sulphur dioxide.

Procedure. The sample containing about 0·25 g of the interfering element, was dissolved in 10 ml of water and the solution was transferred to the column, which was allowed to run at a rate of

1 drop/sec. The column was washed with 100 ml of water, and the combined eluate was adjusted to 25 ml by evaporation and dilution in a graduated flask. The sodium and potassium were determined by the addition technique in the usual way.

Analyses were carried out on samples to which known quantities of sodium and potassium had been added. The recoveries obtained are given in Table VII.

The results were satisfactory, considering the large blank values which had to be taken into account. Erratic results were obtained for iron^{III} salts. In several cases, considerable quantities of iron passed into the eluate. Incomplete absorption was also obtained with chromium.

TABLE VII.—THE RECOVERY OF SODIUM AND POTASSIUM FROM SALTS OF NICKEL, MANGANESE^{II} AND COBALT BY THE PROPOSED METHOD

Compound	Sodium			Potassium		
	Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %
Nickel chloride	0	95	—	0	20	—
	200	290	95	200	180	80
Manganese^{II} sulphate	0	295	—	0	120	—
	800	1025	90	200	280	80
Manganese^{II} acetate	0	205	—	0	370	—
	200	435	115	200	560	95
Cobalt chloride	0	410	—	0	30	—
	200	630	110	200	180	75
Cobalt nitrate	0	2700	—	0	430	—
	200	2900	100	200	570	70

ANALYTICAL PROCEDURES FOR THE DETERMINATION OF TRACES OF SODIUM AND POTASSIUM IN THE PRESENCE OF OTHER METALS

(*a*) *Simple method in the presence of aluminium, beryllium, bismuth, cadmium, lead, magnesium, molybdenum, tin, silver, and zinc*

Reagents

Standard sodium and potassium solutions [see (*b*)].

Procedure

Dissolve a suitable quantity (usually 0·5–1·0 g) of the sample in water or the minimum amount of dilute acid and dilute to 100 ml. To 50 ml of the solution, add 0·5 ml of standard sodium solution (1 ml ≡ 100 μg of Na) and 0·5 ml of standard potassium solution (1 ml ≡ 200 μg of K). Retain the remaining 50 ml of solution. Run each half of the solution through the EEL flame photometer in turn, employing the appropriate filter, and note the galvanometer deflections. If the galvanometer deflection is off the scale repeat the determination with a smaller quantity of the sample.

Calculate the sodium and potassium contents in the following way:

$$\text{Concentration of sodium/potassium (ppm)} = \frac{ad}{(b-a)c}$$

where a = galvanometer deflection due to sample,
b = galvanometer deflection due to sample and standard,
c ≡ concentration of sample (g/100 ml),
and d = concentration of standard (μg/ml).

(b) *Method in the presence of calcium, strontium and cerium*

Reagents

Aluminium nitrate solution: Dissolve 50 g of aluminium nitrate, $Al(NO_3)_3.9H_2O$, in water and dilute to 100 ml with water. Filter if necessary.

Standard sodium solution: Dissolve 0·254 g of dry sodium chloride in water and dilute to 1 litre (1 ml ≡ 100 μg of Na).

Standard potassium solution: Dissolve 0·382 g of dry potassium chloride in water and dilute to 1 litre (1 ml ≡ 200 μg of K).

Procedure

Dissolve a suitable quantity (usually 0·5–1·0 g) of the sample in water or in the minimum amount of 5*N* hydrochloric acid.

For calcium and strontium: Add aluminium nitrate solution in the ratio of 5 ml for every 0·1 g of calcium or strontium present.

For cerium: Add aluminium nitrate solution in the ratio of 6 ml for every 0·1 g of cerium present.

Prepare a blank solution containing the same quantity of aluminium nitrate and dilute the sample and blank solution to 100 ml. Continue as in (*a*), zeroing the flame photometer against the blank solution.

(c) *Method in the presence of manganese, nickel and cobalt*

Reagents

Ammonium acetate solution: Dissolve 20 g of ammonium acetate in 200 ml of water.

EDTA di-ammonium salt: Suspend 10 g of ethylenediaminetetra-acetic acid in 100 ml of water. Stir continuously and add ammonium hydroxide (sp. gr. 0·880) until a clear solution is obtained. Filter before use.

Amberlite IRA-400(Cl) resin, analytical grade.

Standard sodium solution: as in (*b*).

Standard potassium solution: as in (*b*).

Preparation and regeneration of the resin: Make a slurry of the resin and pour this into a 1-cm diameter glass column to a height of about 60 cm. Treat the column successively with the following solutions: 200 ml of 10% w/v ammonium acetate at 1 drop/sec, 100 ml of water at a fast rate, 100 ml of 10% w/v EDTA di-ammonium salt at 1 drop/sec, and 500 ml of water at a fast rate.

Procedure

Dissolve the sample, containing not more than 0·25 g of the interfering metal, in 10 ml of water. If the compound is not water-soluble, dissolve in dilute hydrochloric acid, evaporate to low volume and dilute to 10 ml with water. Transfer the solution to the column and run the column at a rate of about 1 drop/sec. Wash the column with 100 ml of water. Evaporate the eluate and dilute to 100 ml in a graduated flask. Continue as in (*a*).

(d) *Method in the presence of manganese^{VII} and chromium^{VI}*

Procedure

Prepare a 1- × 20-cm column of Amberlite IRA-400(Cl). Wash with water until the eluate is free of sodium and potassium. Dissolve the sample containing not more than 0·5 g of chromium^{VI} or manganese^{VII} in the minimum quantity of water, and transfer the solution to the column.

Run the column at about 1 drop/sec for chromium^{VI} and 2 drops/sec for manganese^{VII}, adding sufficient water to keep the column wet. Wash with 100 ml of water at 2 drops/sec for chromium^{VI} and 4 drops/sec for manganese^{VII}. Reject the used resin. Adjust the eluate to 100 ml by evaporation and dilution in a graduated flask. Continue as in (*a*).

(e) *Method in the presence of uranium*

Reagents

5N sulphuric acid: Dilute 136 ml of sulphuric acid to 1 litre.

0·1N sulphuric acid: Dilute 20 ml of 5*N* sulphuric acid to 1 litre.

5N ammonium carbonate: Dissolve 200 g of ammonium carbonate in a mixture of water and 250 ml of 5*N* ammonium hydroxide. Dilute to 1 litre.

Amberlite IRA-400(Cl): Use the analytical-grade resin.

Standard sodium solution: as in (*b*).

Standard potassium solution: as in (*b*).

Preparation and regeneration of the resin: Prepare a slurry of Amberlite IRA-400(Cl) and pour this into a glass column of internal diameter 1 cm until a height of about 30 cm is reached. Convert the resin to the sulphate form by running 100 ml of 5*N* sulphuric acid through it at about 1 drop/sec. Wash the column with water until the eluate is free of chloride.

The resin should be regenerated immediately after use as uranium is slowly reduced on the resin. Place the resin in a beaker and stir with 50-ml portions of 5*N* ammonium carbonate until the supernatant liquid is no longer coloured. Stir with two 50-ml portions of 5*N* sulphuric acid. Return the resin to the column and wash thoroughly with water.

Procedure

Dissolve the sample, containing not more than 0·5 g of uranium, in 10 ml of 0·1*N* sulphuric acid, and transfer the solution to the column. Run the column at about 1 drop/sec and wash with 100 ml of 0·1*N* sulphuric acid. Adjust the volume of the eluate to 100 ml by evaporation and dilution in a graduated flask. Continue as in (*a*).

Metal	*Procedure*	*Approximate concentration*
Aluminium	Aluminium wire dissolved in 2 : 1 hydrochloric acid: nitric acid.	0·5% Al
Barium	(*a*) Barium acetate dissolved in water; barium precipitated with ammonium carbonate; barium carbonate filtered, dissolved in 5*N* hydrochloric acid. (*b*) Barium carbonate washed with hot water; dissolved in 5*N* hydrochloric acid.	1% Ba
Beryllium	Beryllium sulphate dissolved in water; ammonium carbonate added; beryllium carbonate filtered, dissolved in 5*N* hydrochloric acid.	0·05% Be
Bismuth	Bismuth ingot dissolved in 5*N* nitric acid.	1% Bi
Cadmium	Cadmium chloride dissolved in water, cadmium precipitated with hydrogen sulphide; cadmium sulphide filtered and dissolved in 2 : 1 hydrochloric acid : nitric acid.	1% Cd
Calcium	Known to interfere; not examined.	
Cerium	Ammonium cerium^{IV} nitrate dissolved in water, and cerium precipitated with ammonium hydroxide; cerium^{IV} hydroxide filtered, dissolved in 5*N* hydrochloric acid.	1% Ce
Chromium	(*a*) Ammonium dichromate dissolved in water; passed through Amberlite IRA-400(Cl) column; column washed with water and chromium eluted with 5*N* hydrochloric acid, saturated with sulphur dioxide. (*b*) Chromium^{III} chloride dissolved in water and chromium precipitated with excess ammonium hydroxide; chromium^{III} hydroxide dissolved in 5*N* hydrochloric acid.	1% Cr

Metal	*Procedure*	*Approximate concentration*
Cobalt	(*a*) Cobalt chloride dissolved in water; cobalt precipitated with hydrogen sulphide; cobalt sulphide filtered, dissolved in 2 : 1 hydrochloric acid:nitric acid. (*b*) Cobalt chloride dissolved in 9*M* hydrochloric acid and passed down Amberlite IRA-400(Cl) column. Column washed with 9*M* hydrochloric acid and cobalt eluted with water.[21,22]	1% Co
Copper	(*a*) Copper foil dissolved in 5*N* nitric acid. (*b*) Copper sulphate dissolved in dilute sulphuric acid; solution electrolysed using platinum electrodes; deposited copper dissolved from cathode with 5*N* nitric acid.	1% Cu
Iron	(*a*) Electrolytic iron dissolved in 5*N* hydrochloric acid. (*b*) Iron$^{\text{III}}$ chloride dissolved in hydrochloric acid; iron extracted with 2,2′-dichlorodiethyl ether; ether layer washed with hydrochloric acid; iron extracted with 0·5*N* hydrochloric acid.[23]	1% Fe
Lead	Lead foil dissolved in 5*N* nitric acid.	1% Pb
Magnesium	Magnesium ribbon dissolved in 5*N* hydrochloric acid.	0·5% Mg
Manganese	(*a*) Manganese$^{\text{II}}$ sulphate dissolved in water; excess thioacetamide added; solution boiled; manganese$^{\text{II}}$ sulphide filtered and dissolved in 5*N* hydrochloric acid. (*b*) Electrolytic manganese dissolved in 5*N* hydrochloric acid.	1% Mn
Molybdenum	Ammonium molybdate dissolved in water; solution passed through Amberlite IRA-400(Cl) column; molybdenum eluted with 5*N* ammonium hydroxide; excess evaporated.	0·5% Mo
Nickel	(*a*) Nickel chloride dissolved in water; nickel precipitated with hydrogen sulphide; nickel sulphide filtered and dissolved in 2 : 1 hydrochloric acid:nitric acid. (*b*) Nickel wire dissolved in 2 : 1 hydrochloric acid: nitric acid.	1% Ni
Silver	Silver nitrate dissolved in water; silver precipitated with 5*N* hydrochloric acid; silver chloride filtered and dissolved in 5*N* ammonium hydroxide. Excess *not* evaporated.	1% Ag
Tin	Tin$^{\text{II}}$ chloride dissolved in water acidified with hydrochloric acid; tin precipitated with hydrogen sulphide; tin$^{\text{II}}$ sulphide filtered and dissolved in hydrochloric acid.	1% Sn

Metal	*Procedure*	*Approximate concentration*
Tungsten	Ammonium tungstate dissolved in water; excess 5*N* hydrochloric acid added and solution boiled; tungstic acid filtered and dissolved in 5*N* ammonium hydroxide; excess *not* evaporated.	1% W
Uranium	(*a*) Uranyl nitrate dissolved in 1 : 10 nitric acid containing 70% ammonium nitrate; uranium extracted with diethyl ether,[24] ether layer washed with water and evaporated almost to dryness. (*b*) Uranyl acetate dissolved in water, uranium precipitated with ammonium hydroxide; ammonium di-uranate filtered and dissolved in 5*N* hydrochloric acid. (*c*) Uranyl acetate dissolved in water; uranium extracted with acetyl acetone-carbon tetrachloride mixture at pH 7;[25] uranium extracted with 50 ml of water containing 10 ml of 5*N* hydrochloric acid.	1% U
Zinc	Zinc dissolved in 5*N* nitric acid.	1% Zn

APPENDIX

Methods used for preparation of alkali-free solutions

AnalaR chemicals were used wherever possible, and in each case the excess acid used during the preparation was removed by evaporation almost to dryness, and the residue was dissolved in water.

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Zusammenfassung—Die durch das Hauptmetall verursachten Störungen in der flammphotometrischen Bestimmung von Natrium und Kalium mit einem "EEL"-Flammphotometer werden untersucht. Zahlreiche Metall stören nicht. Methoden zur Ausschliessung der Störungen verschiedener anderer Metalle werden beschrieben wie z.B. Unterdrückung der Flammemmission durch Zusatz von Aluminiumnitrat oder Abtrennung der Störmetalle mittels Ionenaustauscher.

Résumé—Les auteurs ont étudié les interférences dues au métal principal dans le dosage des sels de sodium et de potassium par photométrie de flamme, utilisant un photomètre de flamme "EEL". De nombreux métaux ne gênent pas, ce qui permet de faire un dosage direct. Des méthodes pour éliminer l'interférence de certains autres métaux nécessitent la suppression de leurs émissions de flamme par du nitrate d'aluminium, ou leur séparation par des méthodes d'échange d'ions, avant le dosage du sodium et du potassium.

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THE DETERMINATION OF TRACES OF OSMIUM AND IRIDIUM IN SAMPLES OF PALLADIUM AND PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A method is described for the determination of ultramicro quantities of osmium and iridium in samples of palladium and platinum. In order to avoid self-shielding differences between samples and standards during neutron irradiation, standards have been prepared by the addition of very small known amounts of osmium and iridium to analytical samples. In the analysis of palladium samples the Harwell Pile BEPO has been used as the neutron source. To avoid spurious results due (n,p) and (n,α) reactions, the Pile DIDO has had to be used for neutron-activation of samples of platinum. Each determination requires 0·1 g of sample, and radiochemical separations using carriers have been used to isolate the induced osmium and iridium activities. Results are quoted for the osmium and iridium contents of some pure palladium and platinum samples.

INTRODUCTION

ONE of the most complex problems in experimental inorganic chemistry is the separation of platinum metals in a high state of purity. This is of considerable importance as the electrical and mechanical properties of the metals are markedly affected by minute quantities of impurities. Hitherto, spectrographic and spectrophotometric methods of analysis have been most extensively employed to determine such trace constituents, but in many cases these procedures do not provide sufficient sensitivity.

Neutron-activation analysis permits the determination of many elements in ultramicro quantities, and the application of this method to the determination of traces of osmium and iridium in samples of palladium and platinum is reported here.

Neutron-activation procedures have been used previously for the determination of osmium and iridium in various materials. Smales[1] has reported the determination of iridium in a sample of rhodium. The decay curve of the irradiated rhodium showed two components, 74-day iridium-192 and 19·0-hour iridium-194, and no radiochemical separation was necessary.

Zvyagintsev and Kulak[2] have investigated the determination of iridium and other precious metals in refined silver by activation analysis, and Italian workers[3] have reported semiquantitative methods for iridium in platinum.

Miller[4] has studied the neutron-activation analysis of elements of Group VIII of the periodic table, and he gives considerable information on nuclear reactions of osmium and iridium and the assay of resulting radionuclides. It has been indicated[5] that at the Oak Ridge National Laboratory neutron-activation has been applied to the determination of osmium in iron and palladium and to the determination of iridium in rhodium chloride and palladium. Analyses showed 10–100 ppm of osmium and 4–5 ppm of iridium in samples of palladium.

Neutron-activation has been used in isotope abundance analysis of osmium.[6]

NEUTRON-ACTIVATION OF OSMIUM AND IRIDIUM

Naturally occurring osmium consists of seven isotopes, ^{184}Os (per cent abundance $\theta = 0{\cdot}018$), ^{186}Os ($\theta = 1{\cdot}59\%$), ^{187}Os ($\theta = 1{\cdot}64\%$), ^{188}Os ($\theta = 13{\cdot}3\%$), ^{189}Os ($\theta = 16{\cdot}1\%$), ^{190}Os ($\theta = 26{\cdot}4\%$) and ^{192}Os ($\theta = 41{\cdot}0\%$). Iridium exists as two stable isotopes, ^{191}Ir ($\theta = 38{\cdot}5\%$) and ^{193}Ir ($\theta = 61{\cdot}5\%$). On irradiation with neutrons of thermal energies, osmium and iridium give rise to radionuclides by the following nuclear reactions:

$$^{184}\text{Os} \xrightarrow{n,\gamma} {}^{185}\text{Os}\ (t_{\frac{1}{2}} = 93{\cdot}6\text{ days}) \xrightarrow{EC} {}^{185}\text{Re(stable)}$$

$$\begin{tikzcd}
^{190}\text{Os} \arrow[r, "n{,}\gamma"] \arrow[dr, "n{,}\gamma"'] & ^{191m}\text{Os}\ (t_{\frac{1}{2}} = 14\text{ hr}) \arrow[d, "IT"] & \\
& ^{191}\text{Os}\ (t_{\frac{1}{2}} = 16\text{ days}) \arrow[r, "\beta^-"] & ^{191m}\text{Ir}\ (t\tfrac{1}{2} = 4{\cdot}9\text{ sec}) \arrow[d, "IT"] \\
& & ^{191}\text{Ir (stable)}
\end{tikzcd}$$

$$^{192}\text{Os} \xrightarrow{n,\gamma} {}^{193}\text{Os}\ (t_{\frac{1}{2}} = 30{\cdot}6\text{ hr}) \xrightarrow{\beta^-} {}^{193}\text{Ir (stable)}$$

$$\begin{tikzcd}
^{191}\text{Ir} \arrow[r, "n{,}\gamma"] \arrow[dr, "n{,}\gamma"'] & ^{192m}\text{Ir}\ (t_{\frac{1}{2}} = 1{\cdot}42\text{ min}) \arrow[d, "IT"] & \\
& ^{192}\text{Ir}\ (t_{\frac{1}{2}} = 74\text{ days}) \arrow[r, "\beta_-(95{\cdot}5\%)"] \arrow[dr, "EC(4{\cdot}5\%)"'] & ^{192}\text{Pt (stable)} \\
& & ^{192}\text{Os (stable)}
\end{tikzcd}$$

$$^{193}\text{Ir} \xrightarrow{n,\gamma} {}^{194}\text{Ir}\ (t_{\frac{1}{2}} = 19{\cdot}0\text{ hr}) \xrightarrow{\beta^-} {}^{194}\text{Pt (stable)}$$

Relevant isotopic thermal neutron-activation cross-sections, σ, in barns, are:[7]

^{184}Os	$\sigma < 200$
^{190}Os	$\sigma = 8$ (16 days)
^{192}Os	$\sigma = 1{\cdot}6$
^{191}Ir	$\sigma = 260$ (1·4 min)
	$\sigma = 700$ (74 days)
^{193}Ir	$\sigma = 130$.

A summary of nuclear data for the different radionuclides produced in the nuclear reactions[8] is given in Table I.

It has been estimated[9] that with a thermal neutron flux of 10^{12} neutrons/cm^2/sec, it should be possible under ideal conditions to determine 1×10^{-9} g of osmium utilising 30·6-hr ^{193}Os with 16-day ^{191}Os. The corresponding calculated sensitivity for iridium is 1×10^{-11} g, using 19-hr ^{194}Ir with 74-day ^{192}Ir.

In the present study a comparative procedure involving simultaneous irradiation of samples and standards has been employed. The thermal neutron absorption cross-sections[7] for osmium, iridium, platinum and palladium are considerable, *viz:*

Os	$\sigma = 15{\cdot}3$ barns
Ir	$\sigma = 440$
Pt	$\sigma = 8{\cdot}8$
Pd	$\sigma = 8{\cdot}0$.

TABLE I.—NUCLEAR DATA FOR RADIONUCLIDES PRODUCED FROM OSMIUM AND IRIDIUM BY (n,γ) REACTIONS.

Radionuclide	Half-life	Radiations and energies, *MeV*
^{185}Os	93·6 days	EC; γ 0·07 to 0·88
^{191m}Os	14 hr	IT e^- (γ) 0·074
^{191}Os	16·0 days	β^- 0·143; γ e^- (with ^{191m}Ir) 0·042, 0·129
^{193}Os	30·6 hr	β^-1·14 (40%), 1·06 (33%), 1·00 (5%) 0·86 (12%), 0·68 (10%); γ 0·073 to 0·460
^{192m}Ir	1·42 min	IT e^- (γ) 0·058 (99·9%); β^- (c.0·1%)
^{192}Ir	74·37 days	β^- 0·67, others (95·5%); EC (4·5%); γ 0·316 0·296, 0·308. 0·468 (others)
^{194}Ir	19·0 hr	β^- 2·24 (66%), 1·91 (15%), 0·98 (10%), 0·43 (*ca.*8%); γ 0·33, (others 0·29 to 2·05)

To avoid neutron self-shielding differences between samples and standards, therefore, standards have been prepared by the admixture of very small known quantities of osmium and iridium with analytical samples.

EXPERIMENTAL

Irradiation

Samples of palladium or platinum powder, *ca.* 0·1 g, were accurately weighed and sealed in silica irradiation tubes of 6-mm internal diameter. Standards were prepared by the addition of weighed portions (*ca.* 0·05 g) of standard solutions of osmium (80 mg of Os/litre, as $(NH_4)_2OsCl_6$ in 3*M* HCl) and iridium (20 mg of Ir/litre, as $(NH_4)_2IrCl_6$ in 3*M* HCl) to 0·1-g samples of platinum and palladium in silica irradiation tubes. The liquid was allowed to soak into the metal powder, then carefully evaporated to dryness, after which the tubes were sealed.

Samples, together with standards containing added osmium and iridium, were packed with silica wool in standard aluminium screw-top cans and were sent to the Atomic Energy Research Establishment, Harwell, for neutron-irradiation. In the case of samples of palladium, irradiation was for 1 week in the Pile BEPO with a thermal neutron flux of 10^{12} neutrons/cm^2/sec. Samples of platinum were irradiated for 1 week in a thermal neutron flux of 9×10^{11} neutrons/cm^2/sec in the Pile DIDO (see Discussion).

Radiochemical separation

Following delivery from Harwell after irradiation, the samples and standards were put through a radiochemical procedure to obtain the necessary separation of osmium and iridium radionuclides. Carrier chemistry was used in the procedure.

Osmium was separated by distillation of the tetroxide, OsO_4. Further purification was obtained by precipitation of hydrous OsO_2, which was subsequently reduced to metal, in which form the osmium was counted.

Following the removal of osmium by distillation, iridium was separated from palladium or platinum by precipitation of the latter elements with calomel in the presence of bromide.[10] Further purification of the iridium was obtained by precipitation of hydrous IrO_2 using $NaBrO_3$ and $NaHCO_3$. After dissolving the precipitate in HCl and fuming with $HClO_4$, the iridium was extracted into pyridine[11] and subsequently was precipitated again as the hydrous dioxide. The dioxide was finally reduced to metal, in which form the iridium was counted.

Preparation and standardisation of carriers

Osmium: Dissolve a weighed quantity of pure recrystallised $(NH_4)_2OsCl_6$ in 3*M* HCl to give a solution containing 5 mg of Os/ml.

Pipette 5 ml of the carrier solution into a weighed porcelain crucible placed inside a large Vitreosil Rose crucible. Pass a stream of hydrogen through the Rose crucible cover, and heat gently. When the solution has evaporated, heat strongly for 30 min, continuing the passage of hydrogen. Cool in hydrogen and weigh the residue as Os. (If there are any black particles in the Rose crucible after the ignition these should be transferred to the inner crucible and included with the residue.)

Iridium: Dissolve 2·3 g of pure $(NH_4)_2IrCl_6$ in 6*M* HCl and dilute to 1 litre with 2% HCl.

Pipette 10 ml of the carrier into a 250-ml beaker and evaporate carefully until the volume is reduced to *ca.* 2 ml. Add 15 ml of 16*M* HNO_3 and 5 ml of 70% $HClO_4$ and evaporate until fumes of $HClO_4$ begin to be evolved. Cool and add 20 ml of warm water. Filter through a small paper to remove silica or other insoluble matter and wash the paper well with 5% $HClO_4$. Collect the filtrate and washings in a 250-ml beaker. Dilute to 100 ml and boil for *ca.* 10 min with 10 ml of 5% $Hg(NO_3)_2$ solution and 5 drops of 10% $NaBrO_3$. Digest for a further 10 min on a water-bath. Decant the solution through a Whatman No. 41 paper, rinse the precipitate on to the paper, and wash well with hot water. Place the paper in a weighed porcelain crucible, dry it and impregnate it with a few drops of saturated NH_4Cl solution. Char the paper at a low temperature and heat the residue at 900° for 10 min. Reduce in hydrogen. Brush the metal powder quantitatively into a platinum crucible and treat with 40% HF, then with 6*M* HNO_3. Evaporate to dryness. Transfer the iridium quantitatively to the original porcelain crucible, reduce and cool in hydrogen and weigh as Ir.

Radiochemical separation procedure

Treat each sample and standard in the following manner:

Step 1. Remove a silica irradiation tube from the can, open it at the constriction and transfer the contents quantitatively to a 250-ml Quickfit distillation flask. Wash out the tube thoroughly with hot 6*M* HCl and transfer the washings to the flask. Add 10 ml of standard Ir-carrier, 4 ml of standard Os-carrier, 5 ml of 12*M* HCl and 5 ml of 18*M* H_2SO_4.

Step 2. Connect the distillation flask, fitted with a dropping funnel, to form an osmium distillation apparatus; join the flask to a train of three receivers, the first containing 1% $KMnO_4$, the second and third each containing 100 ml of 2*M* NaOH and 5 ml of methyl alcohol [Note (*a*)]. Connections should be made through Quickfit spherical joints to permit a degree of flexibility. Connect the final receiver to a suction pump to enable a stream of air to be drawn through the entire train. Cool the receivers containing alcohol-NaOH by surrounding them with ice.

Step 3. Add 20 ml of 16*M* HNO_3 to the distillation flask and heat gently until the metal sample has dissolved, then heat strongly. After *ca.* 10 min, heat the receiver containing $KMnO_4$ solution and continue heating until no trace of brown fumes can be seen in the flask [Note (*b*)]. Retain the contents of the second receiver for *osmium determination* and the residue in the distillation flask for *iridium determination.*

Step 4. *Determination of Osmium.* Transfer the alkaline solution from the second receiver to a 250-ml beaker and neutralise approximately with 12*M* HCl. Heat to 60° and neutralise more exactly (green colour using Universal indicator paper) with 4*M* H_2SO_4 and Na_2CO_3 solution. Digest on a water-bath for a few min, and allow the black precipitate of hydrous OsO_2 to settle. Decant off and discard the supernate. Wash the precipitate thoroughly with saturated NH_4Cl solution.

Step 5. Transfer the hydrous OsO_2 as a slurry to a porcelain crucible. Warm gently to remove any liquid, then ignite under hydrogen for 15 min. Cool the residue under hydrogen and brush it on to a tared aluminium counting tray (A.E.R.E. Cat. no. 4-3/1068). Make sure that the distribution of osmium powder on the tray is uniform. Weigh to establish the chemical yield.

Step 6. *Determination of Iridium.* Evaporate the residual solution from the osmium distillation to small volume. Cautiously add 12*M* HCl dropwise until all nitrous fumes cease to be evolved [Note (*c*)].

Step 7. Add 50 ml of water and 2·5 g of solid NaBr and boil. Add Hg_2Cl_2 (in the form of a freshly prepared paste in water) in portions until the solution turns yellow-green. Digest for 10 min on a water-bath.

Step 8. Filter through a Whatman No. 41 paper and wash the precipitate with hot 2% HCl. Retain the filtrate and washings in a 250-ml beaker.

Step 9. Dilute the filtrate to 150 ml with water, boil, and add 10 ml of 10% $NaBrO_3$ solution. Neutralise to the end-point of bromocresol purple with 10% Na_2CO_3 solution. Boil for 10–15 min. Add a further 10 ml of 10% $NaBrO_3$ and adjust to pH 8. Allow the flocculent precipitate of hydrous IrO_2 to settle and transfer it by filtration onto a Whatman No. 41 paper.

Step 10. Wash the precipitate into a 250-ml beaker with H_2O and dissolve it by the addition of 12*M* HCl and heating on a hot-plate. Evaporate the solution to small volume. Add 10 ml of 70%

$HClO_4$ and fume for *ca.* 15 min until the solution turns deep violet-blue in colour. Cool the solution.

Step 11. Add 10 ml of water and 20 ml of pyridine. Place in a separating funnel and add 19*M* NaOH to separate the pyridine layer. Wash the dark blue pyridine phase three times with equal volumes of 6*M* HCl, separating the layers each time with 6*M* NaOH.

Step 12. Add a few drops of 6*M* NaOH to the pyridine layer and evaporate off the pyridine.

Step 13.Take up the residue in 12*M* HCl and transfer to a 250-ml beaker. Evaporate the solution to small volume and add 15 ml of 16*M* HNO_3 and 5 ml of 70% $HClO_4$. Boil until slight fumes of $HClO_4$ begin to be evolved [Note(*d*)]. Cool the solution, add 20 ml of water and filter [Note (*e*)]. Wash the filter paper with warm 5% $HClO_4$. Collect the filtrate and washings in a 250-ml beaker and dilute to 150 ml with water. Boil with 10 ml of 5% $Hg(NO_3)_2$ and 5 drops of 10% $NaBrO_3$ for 10 min. Digest for a further 10 min. Filter through a Whatman No. 44 paper, and wash the precipitate of hydrous IrO_2 thoroughly with hot H_2O followed by saturated NH_4Cl solution.

Step 14. Transfer the paper and precipitate to a porcelain crucible. Char the paper slowly, then heat to 900° for 10 min. Reduce and cool the residue under hydrogen and brush it on to a tared aluminium counting tray (A.E.R.E. Cat. no. 4-3/1068). Make sure that the distribution of the iridium powder on the tray is uniform. Weigh to establish the chemical yield.

Notes

(*a*) The distillation should be performed in an efficient fume-cupboard. OsO_4 is extremely toxic and the third receiver is used as a precaution to prevent any possible escape of the compound.

(*b*) RuO_4 is not formed under the experimental conditions and hence does not contaminate the osmium distillate (see also Forsyth and Morris[18]).

(*c*) HNO_3 must be removed at this stage.

(*d*) This is to remove Cl^-.

(*e*) The filtration is to remove SiO_2 or other insoluble impurities.

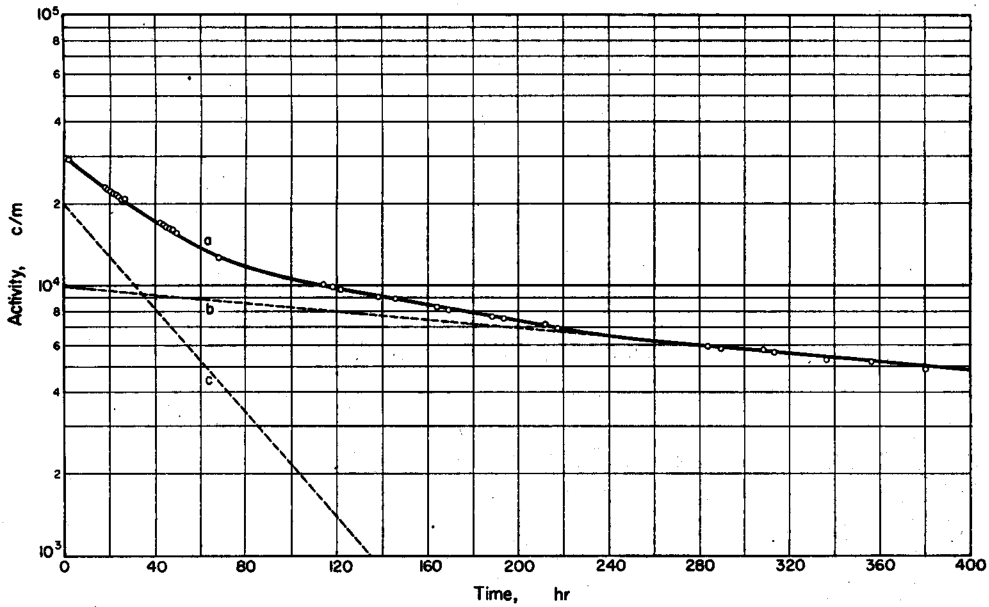

FIG. 1.—Part of a composite decay curve of osmium separated from an analysis standard:
(*a*) Composite decay curve.
(*b*) Osmium-191 activity (observed $t_{\frac{1}{2}}$ = 16·2 ± 1 days)
(*c*) Osmium-193 activity (observed $t_{\frac{1}{2}}$ = 31 ± 1 hr).

Counting of the isolated osmium and iridium

In the present work the separated samples of osmium were counted under a thin end-window Geiger-Müller counter (EHM 2/S), with conventional associated electronic equipment. All measured activities were corrected for paralysis, background, and chemical yield. In order to avoid self-absorption difficulties, the weights of osmium counted from analytical samples and from standards were kept closely similar.

The separated samples of iridium were counted with a NaI(Tl) γ-scintillation counter type 1186A. All measured counting rates were corrected for paralysis, background and chemical yield.

The radiochemical purity of separated osmium and iridium samples was confirmed by decay measurements (*e.g.* see Fig. 1). In the case of iridium, γ-ray spectra were also measured (Fig. 2).

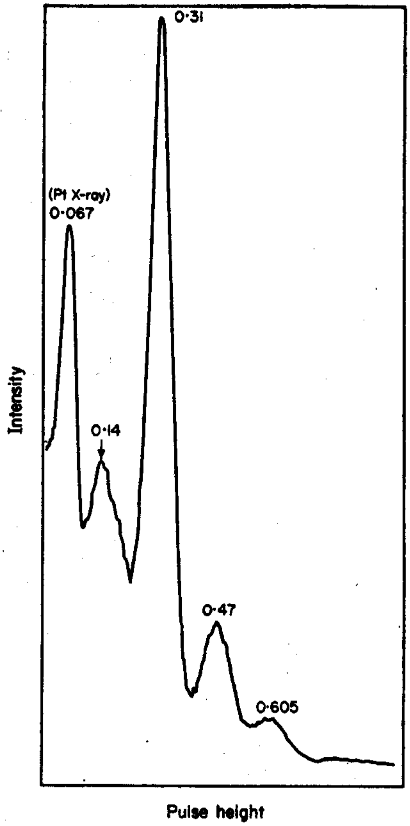

FIG. 2.—γ-Ray spectrum of iridium separated from an analysis sample. Energies in MeV.

RESULTS

In Table II are shown results of analyses of pure samples of palladium and platinum. No osmium or iridium could be detected in these specimens by emission spectrographic analyses.

DISCUSSION

Attention must be given to possible errors caused by conflicting nuclear processes. On neutron-irradiation platinum may give rise to osmium and iridium radio-isotopes by the following nuclear reactions:

^{196}Pt(n,α)^{193}Os (i)
^{194}Pt(n,α)^{191}Os (ii)
^{198}Pt(n,p)^{198}Ir (iii)
^{196}Pt(n,p)^{196}Ir (iv)
^{195}Pt(n,p)^{195}Ir (v)
^{194}Pt(n,p)^{194}Ir (vi)
^{192}Pt(n,p)^{192}Ir (vii)
^{190}Pt(n,p)^{190}Ir. (viii)

TABLE II.—OSMIUM AND IRIDIUM CONTENTS OF SAMPLES OF PALLADIUM AND PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample	Osmium found, *ppm*	Iridium found, *ppm*
Palladium, Pd 1	0·08 0·08	10·4 10·5 11·1 11·1
Platinum, Pt 1	0·30 0·31 0·34 0·36	0·56 0·45 0·53 0·47
Platinum, Pt 2	0·61 0·55	1·45 1·49 1·46 1·50
Platinum, Pt 3	0·85 1·06 0·96 0·96	0·34 0·34 0·28 0·28
Platinum, Pt 4	0·87 0·82	0·38 0·36 0·32 0·32
Platinum, Pt 5	0·25 0·25	3·47 3·43 3·31 3·27
Platinum, Pt 6	0·03 0·03	0·65 0·59
Platinum, Pt 7	0·23 0·22	0·099 0·097

These nuclear reactions are liable to occur with fast neutrons, of which there is a proportion under the irradiation conditions employed in BEPO and DIDO.

With a knowledge of relevant cross-sections and pile fluxes, the disintegration rate of a given radionuclide formed by a (n,γ), (n,p) or (n,α) reaction can be calculated by means of the following equation:

$$A_\tau = \frac{f\sigma\theta WN}{M}\left[1 - \exp.\left(\frac{-0{\cdot}693t}{t_{\frac{1}{2}}}\right)\right]\exp.\left(\frac{-0{\cdot}693\tau}{t_{\frac{1}{2}}}\right)$$

where

A_τ = disintegration rate at a time τ from the end of irradiation, disintegrations/sec,

f = relevant pile neutron flux, neutrons/cm^2/sec,

W = weight of target element, g,
M = atomic weight of the element,
θ = natural abundance of the particular isotope of the element giving rise to the active species,
σ = activation cross-section (cm^2) of the isotope for the particular nuclear reaction,
N = Avogadro number, $6{\cdot}023 \times 10^{23}$,
t = time of irradiation,
and
$t_{\frac{1}{2}}$ = half-life of radioactive product.

Cross-sections for reactions (i)–(viii) with the pile distribution of neutrons may be calculated by the method of Hughes,[13] but since calculated values are only approximate it was decided to investigate experimentally the interference produced by such reactions.

0·1-g Samples of platinum, Pt 1, were analysed using a thermal neutron flux of 1×10^{12} neutrons/cm^2/sec in BEPO, where the corresponding flux of fast neutrons was $1{\cdot}6 \times 10^{11}$ neutrons/cm^2/sec.[14] The following results were obtained for the apparent osmium and iridium contents: Os 0·35, 0·34, 0·34, 0·39, 0·37, 0·38 ppm; Ir 0·70, 0·73, 0·62, 0·59 ppm. It may be noted that these results are higher than the corresponding values shown in Table II where irradiation in DIDO was used. Since the fast neutron flux under the irradiation conditions in DIDO was *ca.* 5×10^8 neutrons/cm^2/sec,[14] it follows that under the analysis conditions a fast flux of $1{\cdot}6 \times 10^{11}$ neutrons/cm^2/sec may give rise to a spurious osmium content of *ca.* 0·03 ppm and a spurious iridium content of *ca.* 0·16 ppm. With the irradiation conditions employed in DIDO interference due to fast neutron reactions may therefore be ignored.

Further nuclear processes which could possibly interfere with the neutron-activation analysis of osmium [reactions (ix) and (x)] and iridium [reactions (xi)–(xiii)] have been shown by calculation[13,15] to be unimportant in the present work:

$$^{191}\mathrm{Ir}(\mathrm{n,p})^{191}\mathrm{Os} \tag{ix}$$

$$^{193}\mathrm{Ir}(\mathrm{n,p})^{193}\mathrm{Os} \tag{x}$$

$$^{197}\mathrm{Au}(\mathrm{n},\alpha)^{194}\mathrm{Ir} \tag{xi}$$

$$^{190}\mathrm{Os}(\mathrm{n},\gamma)^{191}\mathrm{Os} \xrightarrow{\beta^-} {}^{191}\mathrm{Ir}(\mathrm{n},\gamma)^{192}\mathrm{Ir} \tag{xii}$$

$$^{192}\mathrm{Os}(\mathrm{n},\gamma)^{193}\mathrm{Os} \xrightarrow{\beta^-} {}^{193}\mathrm{Ir}(\mathrm{n},\gamma)^{194}\mathrm{Ir}. \tag{xiii}$$

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Zusammenfassung—Eine Methode wird beschrieben, um Ultramikromengen von Osmium und Iridium in Proben von Palladium und Platin zu bestimmen. Um Unterschiede in der Selbstabschirmung von Probe und Standard zu vermeiden, wurden kleine Mengen Osmium und Iridium zu den analytischen Proben zugesetzt. Zur Bestrahlung der Palladiumproben wurde der Harwell-Reactor BEPO als Neutronenquelle herangezogen. Um falsche Ergebnisse durch (n,p) und (n,α) Reaktionen zu vermeiden, wurde der Ofen DIDO zur Neutronenaktivierung von Platinproben herangezogen. Jede Bestimmung benötigt 0·1 g Probe. Radiochemische Trennung unter Heranziehung von Trägermethoden wurden Verwendet, um die induzierten-Osmium- und Iridiumaktivitäten zu isolieren.

Ergebnisse für den Osmium und Iridiumgehalte einiger reiner Palladium- und Platinproben werden mitgeteilt.

Résumé—Les auteurs décrivent une méthode de dosage d'ultramicroquantités d'osmium et d'iridium dans des échantillons de palladium et de platine. Afin d'éviter des différences "d'autoprotection" entre les échantillons et les étalons pendant l'irradiation par les neutrons, les étalons ont été préparés par addition de très faibles quantités connues d'osmium et d'iridium aux échantillons analytiques. Dans l'analyse des échantillons de palladium la pile BEPO de Harwell a été utilisée comme source de neutrons. Pour éviter des résultats erronés dus à des réactions (n,p) et (n,α), la pile DIDO a dû être utilisée pour l'activation par les neutrons des échantillons de platine. Chaque dosage nécessitait 0,1 g d'échantillon, et des séparations radiochimiques utilisant des entraîneurs ont été employées pour isoler les activités induites de l'osmium et de l'iridium. Les résultats sont donnés en teneurs en osmium et en iridium des échantillons de palladium et de platine purs.

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ETHANOL-WATER-HYDROCHLORIC ACID ELUENTS IN ANION-EXCHANGE SEPARATIONS

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Summary—A ternary system of ethanol-water hydrochloric acid has been investigated for the anion-exchange separation of elements which have low adsorption coefficients in aqueous hydrochloric acid solutions. A ternary system is used to express the data from batch distribution coefficients in order to facilitate the prediction of column separation. The anion-exchange separation of manganese from nickel and calcium and the separation of yttrium and scandium has been accomplished.

DURING the course of the investigation of the separation of metals by means of the anion-exchange separation of their chloro-complexes, it became apparent that the addition of water-miscible organic solvents enhanced the adsorption of many of these complexes. An extensive study of the adsorption characteristics of ions from aqueous hydrochloric acid solution[1] has led to many anion-exchange separations of metals.[2–6]

The addition of non-aqueous solvents to increase the adsorption has been considered by several investigators.[7–9] In most cases investigations have been confined to elements which show a considerable adsorption from aqueous hydrochloric acid solutions. It appeared more fruitful to utilise the non-aqueous solvents in order to develop anion-exchange separations of those elements which exhibit low distribution coefficients from aqueous solutions. The purpose of this investigation was to extend the use of ion-exchange separations to those elements which show limited adsorption from aqueous solution. For this reason elements such as iron, copper, and cobalt, which are easily adsorbed from aqueous solution, were automatically excluded from the investigation.

EXPERIMENTAL

Reagents

Anion-exchange resin: Dowex 1 × 8, 200–400-mesh chloride-form resin was used for both the equilibrium studies and the column separations. The resin as received was slurried with water and the fines decanted several times. The resin was then loaded in a large plastic column and washed several times with alternate solutions of 9 *M* and 0·5 *M* hydrochloric acid and with 2·5% hydrofluoric acid. This treatment removes metal impurities from the resin. The resin was washed thoroughly with water in order to remove the acid and subsequently oven-dried at 100°.

Metal solutions: The metal chlorides were used in all cases. In some cases it was necessary to convert oxides or other salts to the chlorides before the equilibrium studies or column separations. The metal chlorides were dissolved in water and standardised by EDTA titrations using established techniques. During the course of the investigation of the ethanol-rich regions and particularly the absolute alcohol composition, it was necessary to prepare standard solutions of the metal chlorides in absolute alcohol.

Ethanol-water-hydrochloric acid mixtures: In order to simplify the representation of data and the preparation of various elution mixtures, the solutions were treated as a ternary phase diagram of ethanol-water-hydrochloric acid. Each solution is made up on the basis of twelve parts in order to simplify the use of concentrated hydrochloric acid in the diagram. Thus a 1 *M* solution of hydrochloric acid represents a mixture of one part of concentrated hydrochloric acid and eleven parts of water and/or ethanol. If two components are specified, a single composition on the ternary is fixed, since the total of parts must equal twelve. In all cases the changes in volume due to mixing are ignored. Admittedly volume changes do take place; however, if one transposes from equilibrium diagrams to column separations and ignores volume changes in both cases, the volume changes which do take place are purely academic.

Measurement of equilibrium coefficients

2·000 ± 0·001 g of dried resin were transferred to 125-ml polyethylene screwcap bottles. The appropriate volumes of sample solution, alcohol, water and hydrochloric acid were added to give a total volume (added) of 120 ml. A minimum ratio of ten to one was maintained between the capacity of the resin and the metal ion added (equivalents), assuming that the adsorbed species was a univalent anion. The bottles were capped slightly below atmospheric pressure by compressing the bottle before tightening the cap, and revolved slowly end-over-end for 12 hr. The polyethylene bottles are convenient for equilibrium studies and by working with a somewhat reduced pressure the danger of losses by leakage is diminished.

After mixing, the contents of the bottle were filtered through a dry filter paper in order to remove the resin, and the metal content of the liquid phase was determined by an EDTA titration of an aliquot. The distribution coefficients D_v were calculated from the formula

$$D_v = \frac{\text{meq metal on resin/ml of resin}}{\text{meq metal in soln/ml of solution}}.$$

Representation of results

The distribution coefficients obtained from the equilibrium studies can be used to predict the behaviour of species in a column separation. For column separations it is desirable to have widely divergent distribution coefficients for the metal ions to be separated. The ion to be eluted from the column should have a low distribution coefficient in order to be eluted from the column in a reasonable volume. The ion to be retained on the resin should have a large distribution coefficient in order to minimise the possibility of contamination.

In order to correlate the distribution coefficients obtained from the ethanol-water-hydrochloric acid system with the data available from aqueous hydrochloric acid solutions the logarithm of the distribution coefficient was used. If one uses the ternary system of co-ordinates for the composition of the aqueous phase and plots the log of the distribution coefficients perpendicular to the plane of the triangle, a curved surface is obtained from which one can observe the log D_v for any liquid composition in the triangle. In practice this becomes complicated because the over-lapping curved surfaces become difficult to correlate in order to select optimum conditions for a separation. Prior experience has indicated that if log D_v is greater than one the constituent is easily retained on the column, whereas log D_v values 0·5 or less represent ions relatively easy to elute. For this reason it appeared convenient to determine the liquid-phase compositions where log D_v was equal to or greater than one. This was accomplished by obtaining log D_v values at systematic points through the region of the ternary system where adsorption was observed. Log D_v values were obtained with constant parts of alcohol and varying ratios of water-hydrochloric acid. These log D_v values were plotted so as to give the log D_v *vs.* water-hydrochloric acid ratio for any given level of alcohol. From these plots it was possible to obtain the compositions of the liquid phase where log D_v is equal to one. If plotted on the three-dimensional curved surface which represents the log D_v values a curve would result which separates the surface where log D_v is equal to one. The curve so obtained was projected onto the ternary system so as to represent in two dimensions the compositions of the system where log D_v equals one. These curves are shown in Fig. 1.

Areas to the left of a curve represent log D_v greater than one, while areas to the right represent log D_v values less than one. It should be noted that Fig. 1 does not represent the complete ternary system, but the HCl—H_2O line in Fig. 1 is at the six parts of alcohol level. It is apparent that only a small portion of the ternary system provides an adequate distribution coefficient to allow the retention of these ions on a column. However, the metal ions shown in Fig. 1 show little or no adsorption from aqueous hydrochloric acid, so the addition of ethanol to the system has a considerable effect. Ions which exhibit strong adsorption from aqueous hydrochloric acid may be expected to show even stronger adsorption in the ternary system.

In order to utilise Fig. 1 to predict conditions for column separations, it is necessary to select a composition which lies within the area bounded by the log $D_V = 1$ curves. The elements whose curves lie to the left of the composition selected will be eluted while those to the right will be adsorbed. It is preferable to use a composition as far away from the curve for the elements to be eluted as is possible without crossing the curves for the elements to be adsorbed.

In addition to the elements which show significant adsorption, there are some elements which show little adsorption even in the ternary system. For example, nickel, calcium and chromium may be separated from the elements shown in Fig. 1 by selecting a composition in the area to the left of the log $D_V = 1$ curve for the element selected.

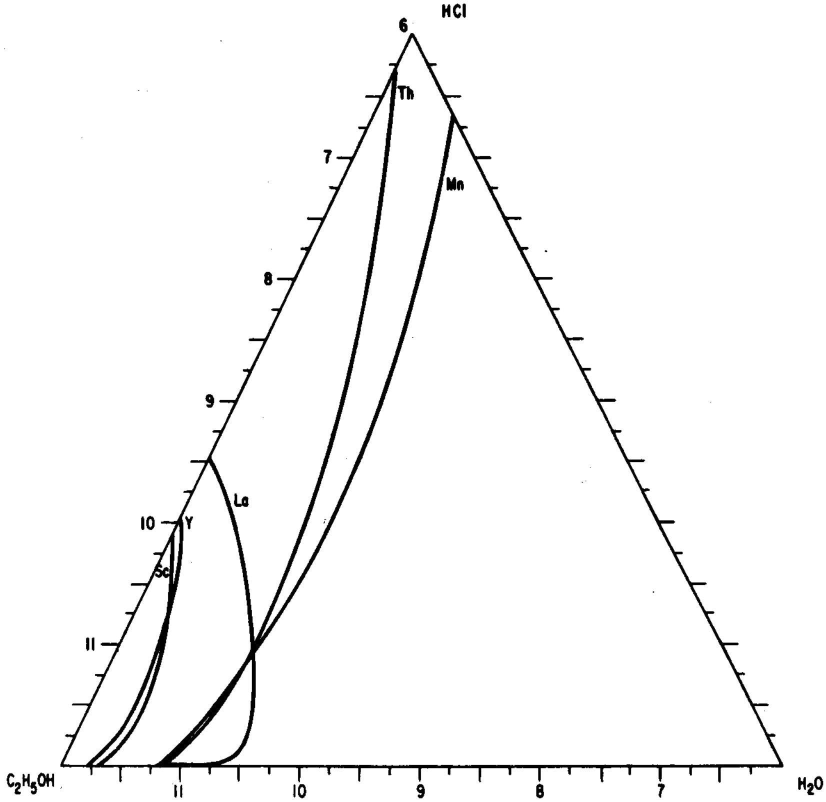

Fig. 1.—Curves of compositions where log D_V is equal to unity.

The adsorption characteristics at the absolute alcohol point are somewhat anomalous and require special mention. In some cases studied a maximum adsorption was noted at a composition near the 11·6 parts of alcohol: 0·2 parts of water: 0·2 parts of hydrochloric acid. The adsorption decreased from this point in all directions. The decrease in adsorption at the absolute alcohol point is particularly interesting in that the changes in the adsorption for yttrium and scandium are sufficiently different to allow a separation. Fig. 1 shows no composition where yttrium and scandium may be separated. The log D_V values are greater than 1, and nearly the same, as one approaches the composition 11·6 parts of alcohol: 0·2 parts of water: 0·2 parts of hydrochloric acid. At the absolute alcohol point scandium shows a sharp decrease in adsorption whereas yttrium shows a sharp increase. In absolute alcohol the log D_V for scandium has decreased from 1·24 to 0·73 while the log D_V for yttrium has increased to a maximum of 2·36. Obviously this difference is adequate for a separation. Thorium, lanthanum and erbium also exhibit a sharp increase at the absolute alcohol point. Manganese decreases similarly to scandium, but the log D_V value remains greater than one.

Column separations

Manganese from nickel or calcium: The columns used contained a resin bed, 1 cm × 10 cm, of Dowex 1 × 8, 200–400 mesh, chloride-form anion-exchange resin. Before introducing the sample solution the resin bed should be equilibrated with the solvent to be used during the elution. The solvent selected for the retention of manganese on the column was 10 parts of ethanol:2 parts of hydrochloric acid which gives a log D_v for manganese of 2·5.

The sample solution of the chlorides was evaporated to a small volume and diluted to 50 ml with the 10:2 solvent. The sample was transferred to a column and nickel or calcium eluted with 100 ml of the 10:2 solvent. Manganese was subsequently eluted with 100 ml of 0·5 *M* hydrochloric acid.

Yttrium from scandium: The columns used contained a resin bed, 6 mm × 47 cm, of Dowex 1 × 8, 200–400 mesh, chloride-form anion-exchange resin. The resin bed was equilibrated with absolute ethanol before adding the sample to the column. The sample solution of the chlorides was evaporated to a small volume and diluted to 50 ml with absolute ethanol. The solution was then transferred to the ion-exchange column. After the solution drained to the resin bed, the scandium was eluted with 150 ml of absolute ethanol. The yttrium was subsequently eluted with 150 ml of 8 parts of ethanol: 2 parts of water: 2 parts of hydrochloric acid.

The determinations were concluded by established EDTA procedures after volatilisation of the solvent.

DISCUSSION

The results which were accumulated in order to construct Fig. 1 were limited to those elements which exhibit limited adsorption in aqueous hydrochloric acid. Elements such as copper, cobalt, iron, zinc, *etc*., which may be strongly adsorbed under appropriate conditions from aqueous hydrochloric acid solutions would be expected to show strong adsorption over much of the ternary system. Although one could construct curves in Fig. 1 for these elements it appears more convenient to use the alcohol-water-hydrochloric acid system only as an auxiliary technique to the well-established aqueous ion-exchange separations. The separation scheme is intended for further separations of those elements which appear in the 7–9*M* aqueous hydrochloric acid eluents in anion-exchange separations. The eluent should be evaporated to a small volume, then sufficient alcohol, water and hydrochloric acid added to attain the appropriate composition on Fig. 1.

In addition to ethanol one may use other miscible solvents such as acetone and isopropyl alcohol. The characteristics of adsorption are modified to some extent, however; ethanol was satisfactory for the separations desired.

The difference in the adsorption characteristics of lanthanum and yttrium is unusual. The log $D_v = 1$ curve for erbium (not shown) is very close to that of yttrium. An investigation of other members of the lanthanide series will be conducted with the possibility of obtaining some separations of mixtures of the rare earths. In the event that a series of log $D_v = 1$ curves for the other rare earths lie between the lanthanum and erbium lines gradient elution techniques should be applicable for the separation of these elements in a high state of purity.

Further investigation of the nature of the adsorbed species for the absolute alcohol solutions is necessary. Since chloride ions are not added in excess one would assume that the chloride necessary for the formation of chloro complex is furnished by the resin:

$$RR_3'N^+Cl^- + LaCl_3 \rightleftharpoons RR_3'N^+LaCl_4^-.$$

Zusammenfassung—Ein ternäres system Äthanol-Wasser-Salzsäure wurde untersucht um die Trennung von Elementen mittels Anionaustauscher zu verbessern, wenn die Absorptionkoeffizinten in wässriger Salzsäure zu nieder sind. Ein ternäres System wurde herangezogen um die Verteilungskoeffizienten auszudrucken, was die Voraussagen über den Wirkungsgrad von Saulentrennungen erleichtert. Trennungen von Mangan von Nickel und Calcium sowie Yttrium von Scandium an Anionenaustauschern wurden ausgearbeitet.

Résumé—Un système ternaire: éthanol-eau-acide chlorhydrique, a été étudié en vue de la séparation par échange anionique d'éléments qui ont de faibles coefficients d'adsorption en solutions aqueuses d'acide chlorhydrique. Un système ternaire est utilisé pour exprimer les résultats à partir des coefficients de partage de l'échantillon afin de faciliter la prévision de la séparation sur colonne. Les séparations par échange anionique du manganèse d'une part et du nickel et du calcium d'autre part, et la séparation de l'yttrium et du scandium, ont été réalisées.

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NON-AQUEOUS SOLVENTS IN ANION-EXCHANGE SEPARATIONS*

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Summary—Distribution coefficients are measured for the partition of metal ions between anion-exchange resin and organic solvent-water mixtures containing hydrochloric acid. The presence of an organic solvent causes metal ions to be taken up at lower hydrochloric acid concentrations. In many cases, distribution coefficients are significantly higher than in water-hydrochloric acid systems. If other conditions are comparable, the order of distribution coefficients in alcohol-water-hydrochloric acid is: isopropyl > ethyl > methyl alcohol. Column separations of metal ion mixtures can be carried out by eluting with alcohol-water-hydrochloric acid mixtures of different compositions. Successful separations of a number of mixtures are reported.

INTRODUCTION

THE separation of metals as chloro complexes from aqueous hydrochloric acid solutions using anion-exchange columns is now a well-established and valuable analytical procedure.[1–8] In this method, metals that form anionic chloro complexes are taken up from strong hydrochloric acid solutions; other metals pass through the column. Then the metals on the column are eluted one or two at a time using aqueous solutions of hydrochloric acid that are progressively more dilute.

It was observed that metals are taken up strongly and at lower hydrochloric acid concentrations if an appreciable amount of a water-miscible organic solvent is added to the aqueous hydrochloric acid. The purpose of the present work was to study the anion-exchange behaviour of metal chloro complexes in partly non-aqueous media. The primary aim was to find conditions that would improve the convenience and broaden the scope of this type of analytical separation.

Katzin and Gebert[9] studied the absorption of lithium chloride, lithium nitrate, cobalt chloride and nickel nitrate on chloride- and nitrate-form anion-exchange resins from acetone solution. They noted that the whole salt is adsorbed and suggested that the salts might be taken up as complex anions. On the other hand, Davies and Owen[10] postulated that the salts are adsorbed by the resin by a solvent extraction process. Tuck and Welch[11] found that the uptake of plutonium^{IV} by an anion-exchange resin from a nitric acid-diethyleneglycoldibutyl ether solution is the result of anionic complex formation.

In the anion-exchange separation of sulphate, sulphite, thiosulphate, sulphide, selenite and tellurite, Iguchi[12,13] found that the addition of alcohol to the eluting agent increased the adsorbabilities of all but the selenite and tellurite. Burstall *et al.*[14] eluted gold (adsorbed as the cyanide) from an anion-exchange column using an acetone eluent containing 5% hydrochloric acid and 5% water. Korkisch *et al.*[15] separated uranium^{VI} from certain other metals on a chloride-form anion-exchange

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column using a solution of hydrochloric acid in mixed water and ethyl alcohol. The addition of 10 to 25% methyl alcohol to an aqueous hydrochloric acid eluent has been found to improve the anion-exchange separation of zinc and cadmium.[16] Recently Kojima[17,18] and Yoshino and Kurimura[19] studied the anion-exchange behaviour of several of the transition elements in mixed solvents containing hydrochloric acid. Distribution coefficients of metal ions were measured in various combinations of hydrochloric acid, water and organic solvent, and the results were compared with the distribution coefficients found in aqueous hydrochloric acid solutions by Kraus and Nelson.[1,2] In all cases the incorporation of a non-aqueous solvent in the mixture caused the distribution coefficients to be higher. An elution scheme for several metal ions was devised, and the method was applied to the determination of aluminum and copper in certain zinc alloys.

EXPERIMENTAL

Reagents

Anion-exchange resin: Dowex 1 × 8 "analysed reagent" resin, either 100- to 200-mesh or 200- to 400-mesh. The finer mesh resin gives somewhat sharper separations and was used in most of the column separations. Before use, backwash the resin to remove the very fine particles, then wash a column of resin with 2 to 2·5*M* perchloric acid to remove metallic impurities. Wash with water, then convert the resin to the chloride-form by successive washing with 2 to 2·5*M*, 1*M*, and 0·005*M* hydrochloric acid. Wash with water, then remove the water by suction filtration. Wash the resin with absolute alcohol, then with acetone, and allow it to air-dry. The air-dried resin has a water content of 5 to 10% by weight.

EDTA, (disodium dihydrogen ethylenediaminetetra-acetate dihydrate): Prepare a 0·05*M* stock solution from reagent-grade salt. Standardise by titration of zinc^{II} from primary standard zinc metal or by titration of cadmium^{II} from the primary standard, HCdV.[20] Naphthyl azoxine indicator is recommended for the standardisation.[20,21]

Metal salts: Reagent grade metal chlorides were used when available. Rare-earth, yttrium and scandium chloride solutions were prepared by dissolving the oxides in hydrochloric acid. Thorium^{IV} and uranium^{VI} nitrates, which were converted to chlorides by anion-exchange, were used, and vanadium^{IV} was used as the sulphate. In a few experiments metal perchlorates were employed. The solutions were 0·05*M* to 0·1*M*.

Organic solvent-water-hydrochloric acid mixtures: Mixtures were prepared so that the amount of organic solvent and water was expressed as percentage by volume and the hydrochloric acid concentration as molarity. For example, 1 litre of 1*M* hydrochloric acid in 80% isopropyl alcohol is prepared as follows: Mix together 800 ml of isopropyl alcohol, 83 ml of concentrated hydrochloric acid and 117 ml of water. Disregard any changes in volume due to mixing.

Procedures

Macro amounts of most metal ions were determined by titration with EDTA. Conditions are summarised in Table I. Iron^{III}, chromium^{III} and uranium^{VI} were determined by standard redox methods.

Micro amounts of metal ions were determined by colorimetric methods: copper^{II} with neocuproine,[28] zinc^{II} with zincon,[29] thorium^{IV} with thorin,[30] uranium^{VI} with arsenazo,[31] bismuth^{III} with thiourea,[32] and iron^{II} with 1:10-phenanthroline.[33]

Measurement of distribution coefficients

Weigh accurately approximately 1 g of air-dried anion-exchange resin into a 125-ml glass-stoppered Erlenmeyer flask. Pipette into the flask 4 ml of metal salt solution and 50 ml of the appropriate organic solvent-water-hydrochloric acid mixture. Stopper the flask and shake for 12 to 18 hr (80% or less of organic solvent) or 22 to 32 hr (more than 80% organic solvent) at 24° ± 1°. Pipette an aliquot from the supernatant liquid, evaporate the acid and organic solvent, and determine the metal ion content by an appropriate analytical method. Determine accurately the water content of the resin and calculate the distribution coefficients on a dry weight basis.

TABLE I.—TITRATION OF METAL IONS WITH EDTA

Ions titrated	pH	Indicator	Reference
Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}	5.5–6·5	Naphthyl azoxine	21
Mn^{2+}	10	Eriochrome Black T	22
VO^{2+}	5·5–6·5	Naphthyl azoxine (back-titrated with Zn^{2+})	23
Rare earth^{3+}, Y^{3+}	5·5–6·5	Arsenazo	24
Th^{4+}	1·7–3·0	Arsenazo	24
Sc^{3+}	3·0–4·5	Methylthymol blue	22
Bi^{3+}	1·3–2·0	Thiourea	25
Zr^{4+}	1·3–2·0	Thiourea (back titrated with Bi^{3+})	26
Ca^{2+}	10	Thymolphthalexone	27
Mg^{2+}	10	Eriochrome Black T	22

Separation of mixtures

Prepare a sample mixture by pipetting into a beaker known amounts of standard metal salt solutions. Carefully evaporate the sample mixture nearly to dryness. Add 5 ml of 0·3*M* hydrochloric acid in 97% ethyl alcohol. When the residue is dissolved, transfer the sample to an anion-exchange column using 0·3*M* hydrochloric acid in 95% ethyl alcohol as a rinse solution. Use an ion-exchange column having an inside diameter of either 12 mm or 22 mm; the height of Dowex 1 × 8 resin bed for various separations is indicated in Tables II, III, IV. Elute the various sample constituents from the column with the types and quantities of eluent indicated in Tables II, III, IV with a flow rate of 0·25 to 0·33 ml/min. Evaporate the effluent fractions collected, and determine the amount of metal salt present in each effluent fraction by an appropriate titrimetric procedure.

MEASUREMENT OF DISTRIBUTION COEFFICIENTS

Measurement of distribution coefficients of various metal ions over a wide range of conditions is a good way to avoid choosing eluting conditions for column separations by a strictly trial and error method. The batch distribution coefficient, D, is defined:

$$D = \frac{\text{mequiv. metal on resin/g of dry resin}}{\text{mequiv. metal in solution/ml of solution}}$$

Although this distribution coefficient is measured on a batch basis, it can be used to predict elution behaviour for metals eluted from an ion-exchange column. To separate two substances, conditions should be selected such that the distribution coefficient of one is low (preferably 1 or less) so that elution from the column will be rapid. The distribution coefficient of the other substance under the same conditions should be as large as possible so that this substance will be tightly held by the column.

In aqueous hydrochloric acid solution, the distribution coefficient of most metal ions in contact with anion-exchange resin increases as the concentration of hydrochloric acid is increased. After a certain concentration of hydrochloric acid is attained, the distribution coefficient remains about the same or decreases somewhat with further increases in hydrochloric acid concentration. In partly non-aqueous solutions of hydrochloric acid, two factors cause an increase in the value of D; an increase in hydrochloric acid concentration, or an increase in the proportion of non-aqueous solvent in the water-non-aqueous solvent mixture. In solvent mixtures containing an appreciable amount of non-aqueous solvent, a D value sufficiently high to assure quantitative uptake of a substance on an ion-exchange column occurs at a much lower hydrochloric acid concentration than in completely aqueous systems. Also, the maximum distribution coefficient obtainable in partly non-aqueous systems containing hydrochloric acid is frequently much higher than is possible in aqueous hydrochloric acid solutions. The distribution of manganese^{II} between chloride-form anion-exchange resin and hydrochloric acid solution is an outstanding illustration of the latter. In aqueous hydrochloric acid, the distribution coefficient is always less than 10; in alcohol-hydrochloric acid systems containing only a little water a distribution coefficient of several thousand can be realised.

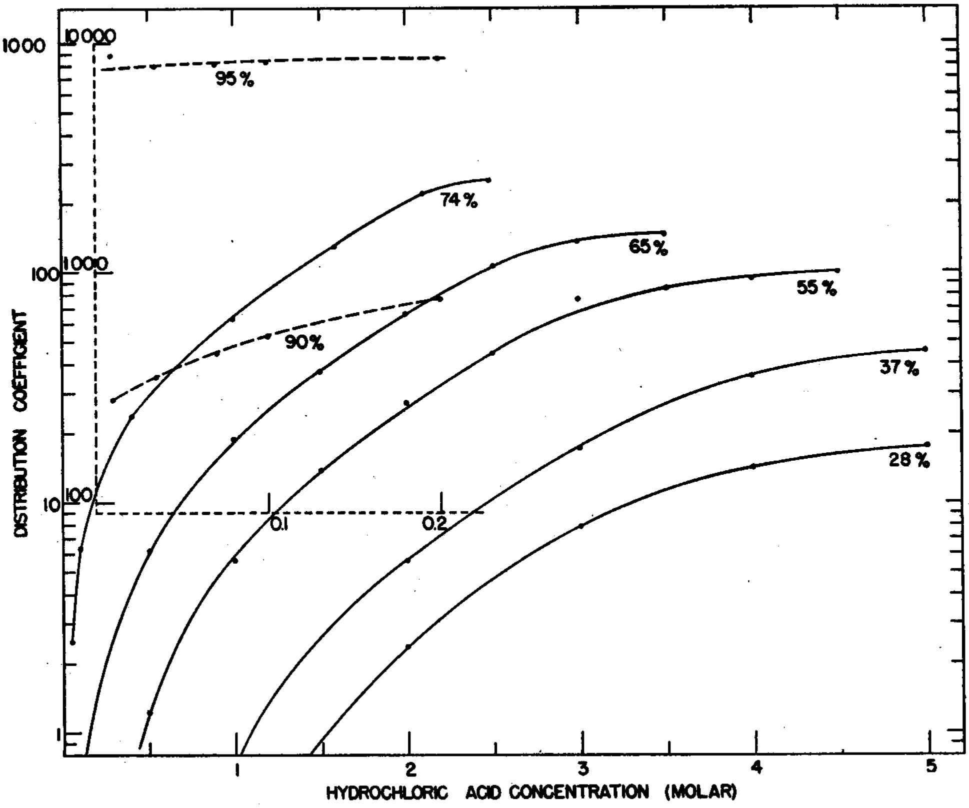

FIG. 1—Distribution coefficients of copper^{II} chloride in various concentrations of isopropyl alcohol *vs.* hydrochloric acid concentrations.

In Fig. 1 the distribution coefficient for copper^{II} is plotted as a function of hydrochloric acid concentration at several isopropyl alcohol-water solvent compositions. It will be noted that the presence of an increasing proportion of isopropyl alcohol has a pronounced effect on the distribution coefficient. In Figs. 2–5, distribution coefficients of other metals are plotted as a function of hydrochloric acid for solvents containing different percentages of isopropyl alcohol.

The effect of different organic solvents on the ion-exchange behaviour of various metal ions was studied. Fig. 6 shows that the various organic solvents studied have about the same effect on the distribution coefficients for copper when the solvent contains an appreciable proportion of water. However, when the solvent contains less than 10 or 15% water, the difference in D in changing from one organic solvent to

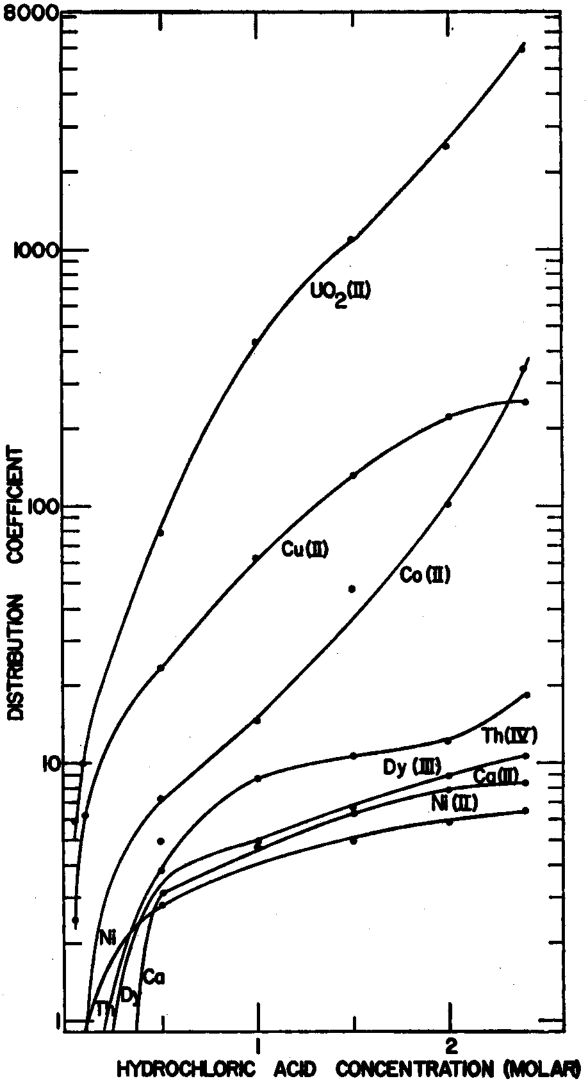

FIG. 2—Distribution coefficients of metal chlorides *vs.* hydrochloric acid concentration in 74% isopropyl alcohol.

another is more pronounced. The distribution coefficients of copper as a function of hydrochloric acid concentration for several solvents are plotted in Fig. 7. Distribution coefficients for several metal ions are plotted in isopropyl alcohol, ethyl alcohol and methyl alcohol in Figs. 8–10. In Figs. 11 and 12, distribution coefficients for various metals are plotted as a function of ethyl alcohol concentration for solutions that are 0·3*M* in hydrochloric acid.

In these figures the concentration of hydrochloric acid is kept low for two reasons. When the proportion of non-aqueous solvent in the mixture is high, only a low concentration of hydrochloric acid is required for metals that form chloro complexes to have high distribution coefficients. Also, the use of much higher concentrations of

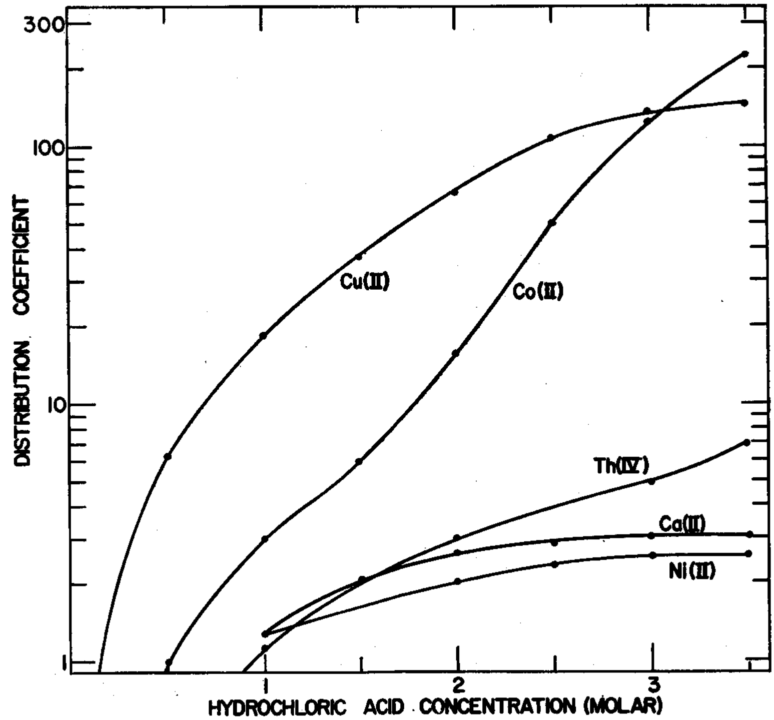

FIG. 3—Distribution coefficients of metal chlorides *vs.* hydrochloric acid concentration in 65% isopropyl alcohol.

hydrochloric acid would make it impossible to maintain the desired concentration of non-aqueous solvent and still use concentrated aqueous hydrochloric acid in preparing the solvent mixture.

Figs. 8–10 show that the distribution coefficients of the metal ions studied are higher in ethyl alcohol than in methyl alcohol, and are still higher in isopropyl alcohol. By mixing the alcohols in varying proportions and keeping the hydrochloric acid concentration constant, a gradual transition of D values from one pure alcohol to another is possible. Figs. 13 and 14 show the distribution coefficients for several metal chlorides in methyl alcohol-isopropyl alcohol and methyl alcohol-ethyl alcohol, respectively.

SEPARATIONS

The batch distribution coefficient, D, can be used to calculate the volume of eluting agent required to elute a metal ion from a given ion-exchange column. The relationships used in such a calculation are as follows:

$$D = D \times \frac{\text{g of resin}}{V}$$

$$U^* = V(D_V + 1)$$

where D is the batch distribution coefficient, D_V is a volume distribution coefficient, V is the interstitial volume (ml) of the resin bed, and U* is the volume (ml) of eluent required to elute a metal ion to a point where the effluent from the column has the

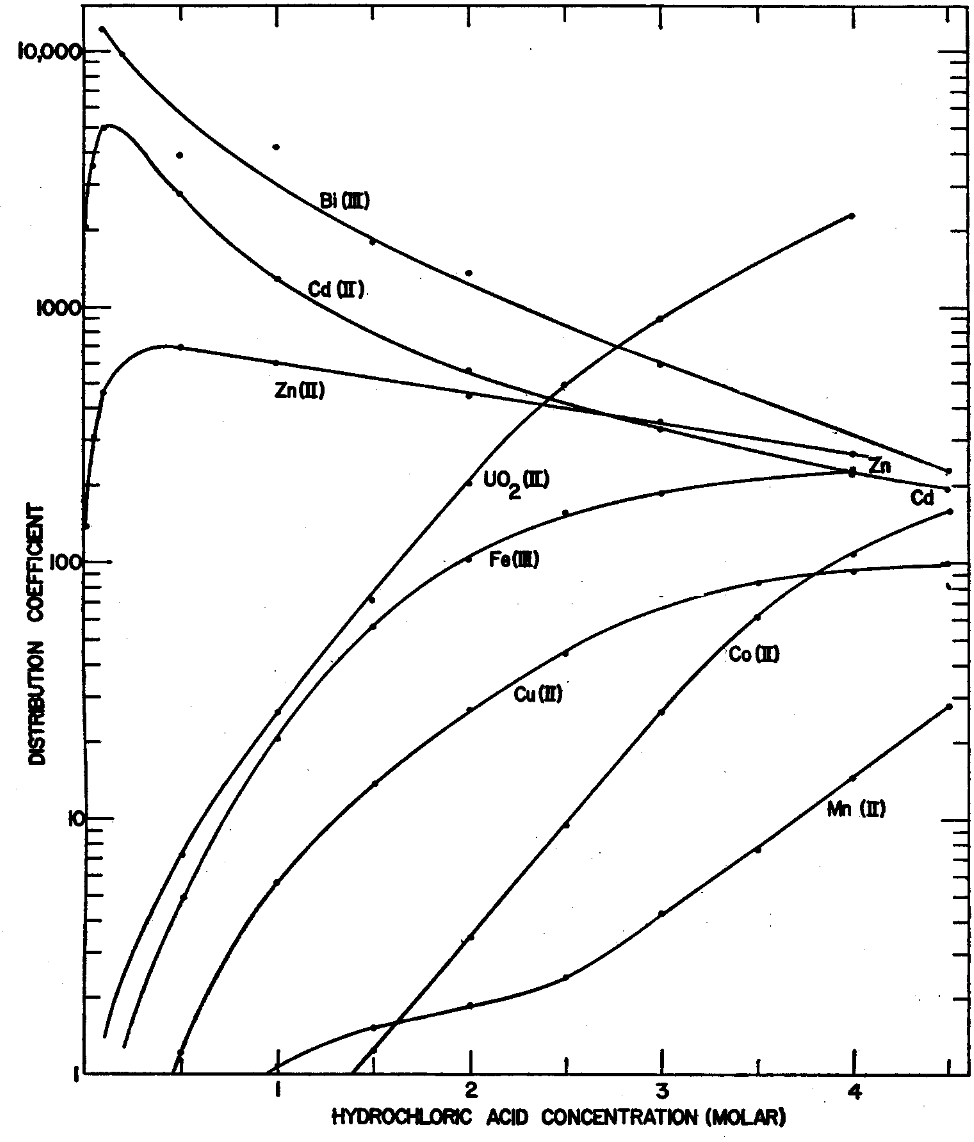

FIG. 4—Distribution coefficients of metal chlorides *vs.* hydrochloric acid concentration in 55% isopropyl alcohol. High adsorption group.

maximum concentration in the metal ion eluted. The volume of eluent required to elute *all* of a metal ion depends on the band width of the metal ion eluted. A good discussion of the selection of column dimensions and operating conditions, when the distribution coefficients of the substances to be separated are known, is given by Cornish.[34]

In the present work, batch distribution coefficients served as a valuable guide in selecting conditions for column separations. However, the volume of solution required to elute various ions from a column was always determined by collecting actual fractions from a column and analysing the fractions. Under the conditions used, this

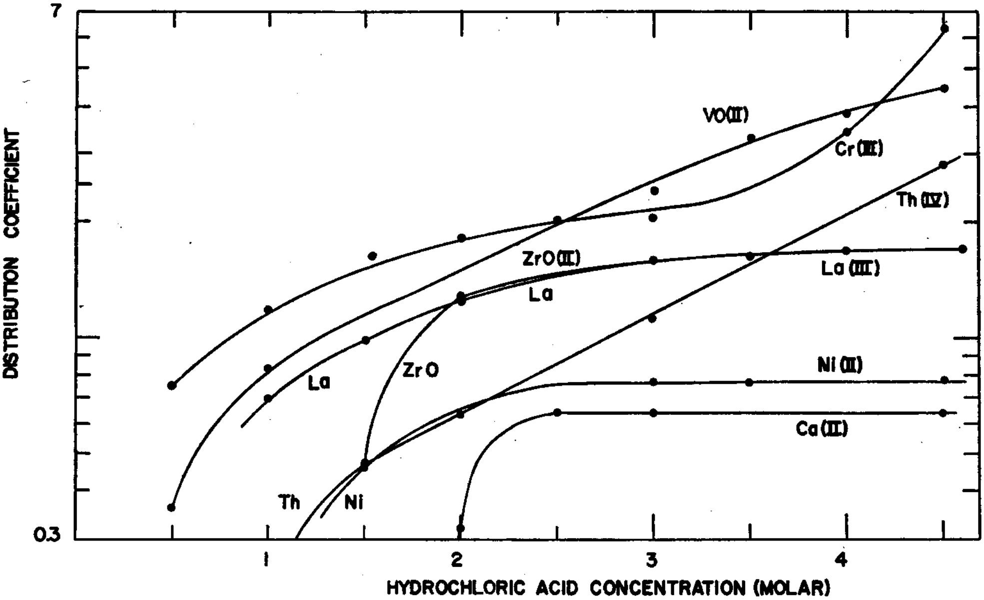

FIG. 5—Distribution coefficients of metal chlorides *vs.* hydrochloric acid concentration in 55% isopropyl alcohol. Low adsorption group.

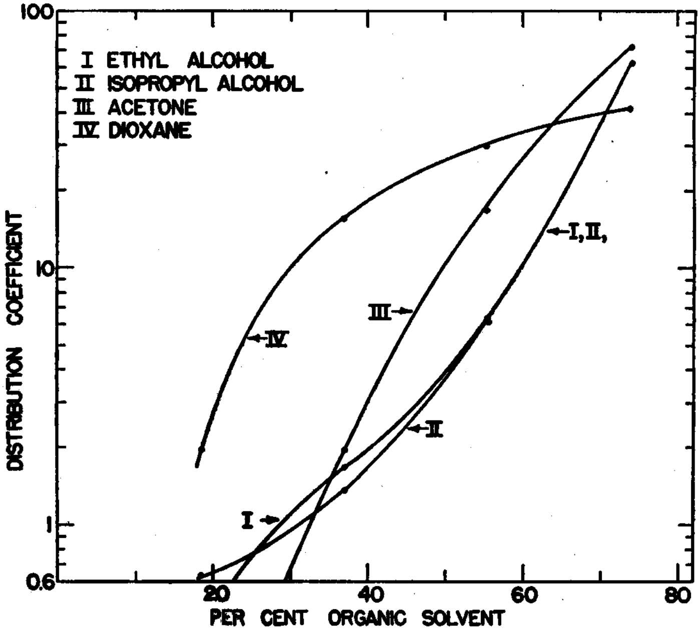

FIG. 6—Distribution coefficients of copper^{II} chloride in 1*M* hydrochloric acid *vs.* varying percentage of organic solvent.

was found to be much more reliable than simply calculating the required volume of eluent from the distribution coefficients.

To separate two metal ions on an anion-exchange column, a solvent composition and hydrochloric acid concentration is chosen such that one metal will be rapidly

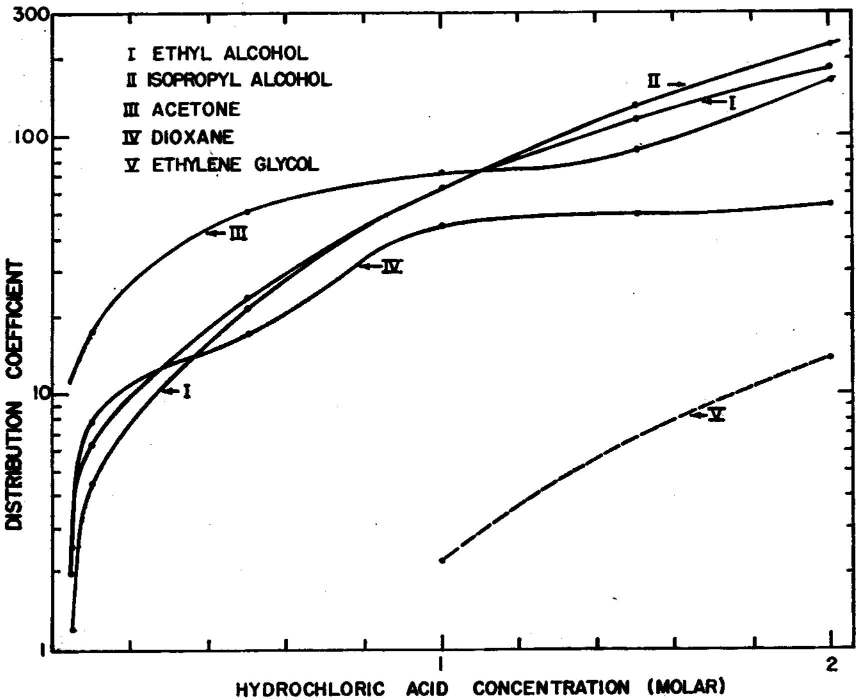

FIG. 7—Distribution coefficients of copper^{II} chloride in 74% organic solvent *vs.* hydrochloric acid concentration.

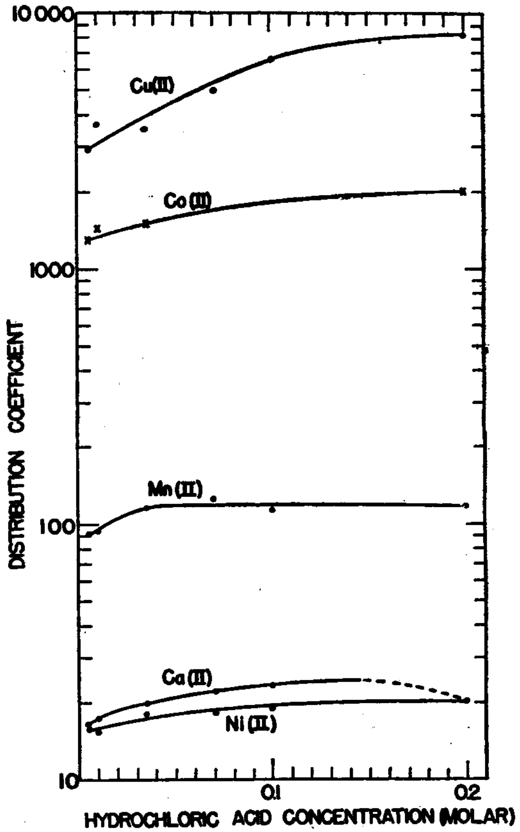

FIG. 8—Distribution coefficients of some metal ions in 96% isopropyl alcohol *vs.* hydrochloric acid concentration.

eluted from the column (D should be low, preferably 1 or below) while the other metal ion has a high D and is tightly held by the column. When several metal ions are to be separated from each other, the scheme is to choose different conditions for successive elutions so that only one metal ion is eluted by each eluting agent. In selecting the composition of eluting agent, we have three variables to work with: the non-aqueous solvent, concentration of non-aqueous solvent in the non-aqueous-water mixture, and concentration of hydrochloric acid.

In alcohol-water mixtures containing a high proportion of alcohol, only a low concentration of hydrochloric acid is required for metal ions to be strongly taken up by an anion-exchange column. As shown in Figs. 7–10 the distribution coefficients of most metals change little with moderate changes in hydrochloric acid concentration. However, inspection of Figs. 11 and 12 reveals that changes in the alcohol content of the solvent affect the D values of metal ions to varying degrees. Thus one elution scheme is based on the use of a series of eluents with a constant hydrochloric acid concentration (0·3*M*), but with decreasing proportions of alcohol. Ethyl alcohol was chosen because the D values of the "non-adsorbable" metal ions such as nickel^{II} and calcium^{II} are too high in isopropyl alcohol (see Fig. 8). Methyl alcohol was not chosen because D values for "adsorbable" metal ions are significantly lower than in ethyl alcohol (Figs. 9 and 10).

The ethyl alcohol elution scheme is as follows:

Sample is added to column in 95% ethyl alcohol-0·3*M* HCl.
Ni^{II} is eluted with 82% to 95% ethyl alcohol-0·3*M* HCl.
Mn^{II} is eluted with 72% to 82% ethyl alcohol-0·3*M* HCl.
Co^{II} is eluted with 72% ethyl alcohol-0·3*M* HCl.
Cu^{II} and Fe^{III} are eluted with 40% ethyl alcohol-0·3*M* HCl.
Zn^{II} is eluted with 0·005*M* aqueous HCl.

Examples of quantitative column separations using this scheme are given in Table II. In some instances the composition of the sample was such that the elution of one of the sample constituents could be accomplished using a lower concentration of ethyl alcohol than stated in the preceding scheme.

Several separations are not possible using this elution scheme. Uranium^{VI}, copper^{II} and iron^{II} can be separated only as a group. Nickel^{II}, calcium^{II}, vanadium^{IV} and chromium^{III} can also be separated only as a group. Manganese^{II} can be separated from this latter group, but the separation is lengthy and only moderately successful. Separation of manganese^{II} from cobalt is not possible.

At higher ethyl alcohol concentrations, tailing of the elution bands is a problem. Tailing of nickel^{II} when eluted with 0·3*M* hydrochloric acid in 95% ethyl alcohol is particularly bad. When nickel is eluted with 0·3*M* hydrochloric acid-82% ethyl alcohol, the tailing is lessened but is still something of a problem. An attempt was made to eliminate tailing by making the 0·3*M* alcoholic solution of hydrochloric acid up to 0·1*M* in perchloric acid. This speeded up all elutions and diminished tailing of the nickel somewhat, but the over-all improvement was not sufficient to recommend the use of perchloric acid in the eluents.

Another elution scheme uses isopropyl alcohol instead of ethyl alcohol (see Figs. 2–5). In this method the isopropyl alcohol concentration is held constant at 55%, and the concentration of hydrochloric acid is varied. The elution scheme is as follows:

Sample is added to the column in 0·3*M* HCl-95% ethyl alcohol.

Table II.—Separation and analysis of synthetic metal ion mixtures on Dowex 1 × 8, 200- to 400-mesh, chloride-form resin. Metals appear in the order of elution with the amount of wash solution included with the first eluted metal.

Metal mixture (column dimensions) and eluting agent	Taken, *mg*	Found, *mg*
Ni$^{\mathrm{II}}$-Cu$^{\mathrm{II}}$ (3 × 1·1 cm)		
Ni 22 ml 95% EtOH-0·3*M* HCl		
10 ml 74% EtOH-0·3*M* HCl	7·17	7·17
Cu 15 ml 40% EtOH-0·3*M* HCl	7·07	7·01
Ni$^{\mathrm{II}}$-Cu$^{\mathrm{II}}$-Zn$^{\mathrm{II}}$ (3 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
9 ml 74% EtOH-0·3*M* HCl	7·17	7·17
Cu 15 ml 40% EtOH-0·3*M* HCl	7·07	7·02
Zn 40 ml 0·005*M* aqueous HCl	7·15	7·16
Mn$^{\mathrm{II}}$-Cu$^{\mathrm{II}}$ (3 × 1·1 cm)		
Mn 2 ml 95% EtOH-0·3*M* HCl		
11 ml 74% EtOH-0·3*M* HCl	7·16	7·13
Cu 15 ml 40% EtOH-0·3*M* HCl	7·07	7·02
Ni$^{\mathrm{II}}$-Mn$^{\mathrm{II}}$-Cu$^{\mathrm{II}}$ (3 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
41 ml 95% EtOH-0·3*M* HCl	7·17	7·11
Mn 10 ml 72% EtOH-0·3*M* HCl	7·16	7·12
Cu 25 ml 0·005*M* aqueous HCl	7·07	7·02
Ni$^{\mathrm{II}}$-Co$^{\mathrm{II}}$ (6 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
13 ml 82% EtOH-0·3*M* HCl	7·17	7·23
Co 15 ml 40% EtOH-0·3*M* HCl	7·64	7·62
Ni$^{\mathrm{II}}$-Co$^{\mathrm{II}}$-Cu$^{\mathrm{II}}$-Zn$^{\mathrm{II}}$ (6 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
12 ml 82% EtOH-0·3*M* HCl	7·17	7·20
Co 17 ml 72% EtOH-0·3*M* HCl	7·64	7·62
Cu 15 ml 40% EtOH-0·3*M* HCl	7·07	7·04
Zn 40 ml 0·005*M* aqueous HCl	7·15	7·20
Co$^{\mathrm{II}}$-Fe$^{\mathrm{III}}$ (3 × 1·1 cm)		
Co 2 ml 95% EtOH-0·3*M* HCl		
10 ml 72% EtOH-0·3*M* HCl	7·64	7·62
Fe 23 ml 40% EtOH-0·3*M* HCl	6·90	6·92
Ni$^{\mathrm{II}}$-Co$^{\mathrm{II}}$-Fe$^{\mathrm{III}}$-Zn$^{\mathrm{II}}$ (6 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
13 ml 82% EtOH-0·3*M* HCl	7·17	7·21
Co 15 ml 70% EtOH-0·3*M* HCl	7·60	7·63
Fe 20 ml 40% EtOH-0·3*M* HCl	6·90	6·90
Zn 40 ml 0·005*M* aqueous HCl	6·91	6·82
Ni$^{\mathrm{II}}$-Fe$^{\mathrm{III}}$-Bi$^{\mathrm{III}}$ (3 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
6 ml 72% EtOH-0·3*M* HCl	7·17	7·17
Fe 12 ml 40% EtOH-0·3*M* HCl	6·90	6·88
Bi 25 ml 1*M* aqueous H_2SO_4	6·90	6·82

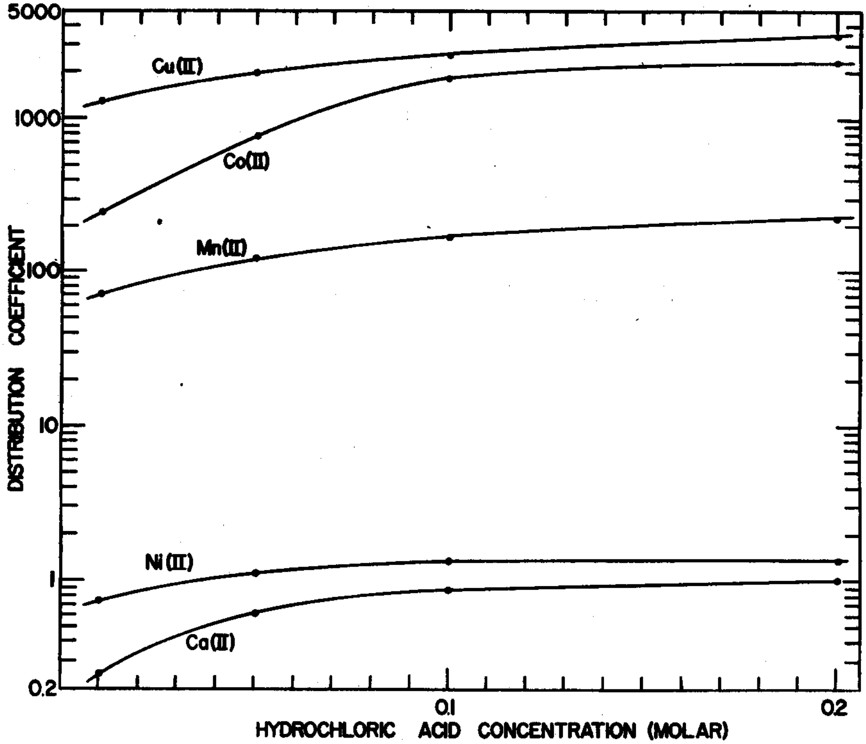

FIG. 9—Distribution coefficients of some metal ions in 96% ethyl alcohol *vs.* hydrochloric acid concentration.

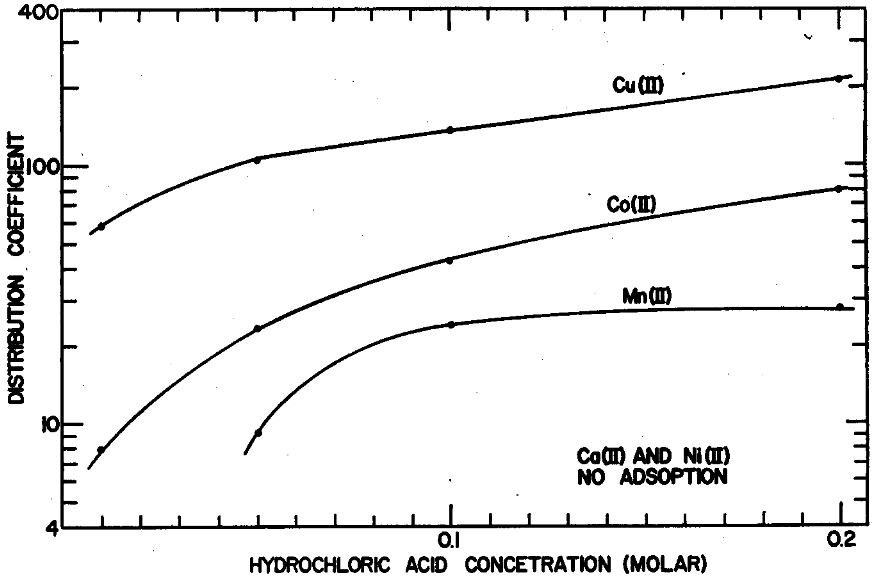

FIG. 10—Distribution coefficients of some metal ions in 96% methyl alcohol *vs.* hydrochloric acid concentration.

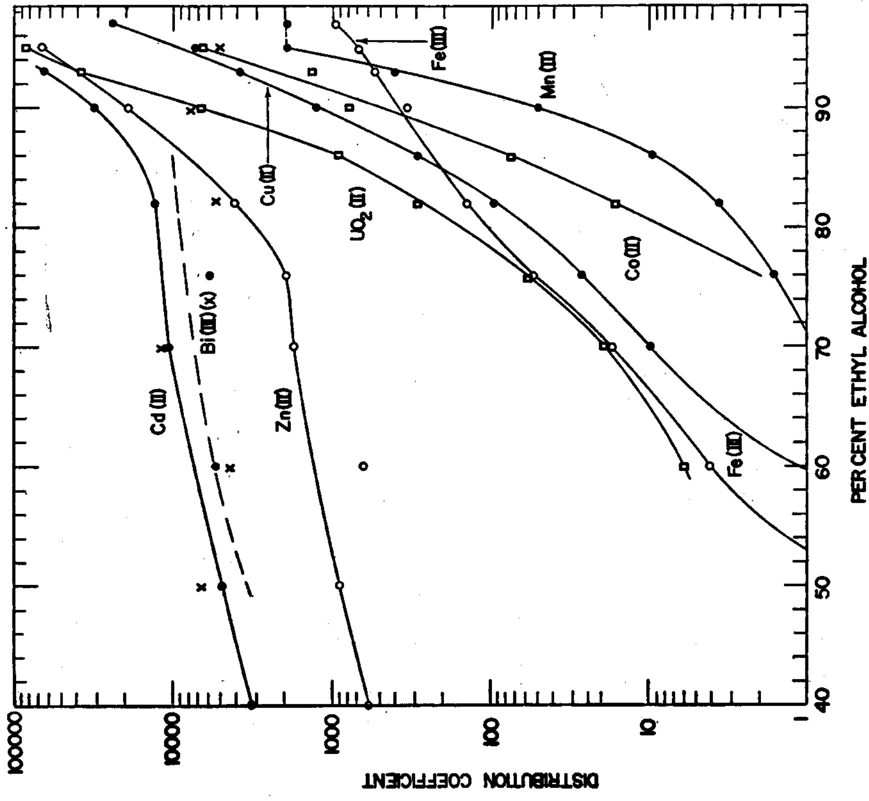

FIG. 11—Distribution coefficients of metal chlorides in 0·3M hydrochloric acid *vs.* percentage of ethyl alcohol. High adsorption group.

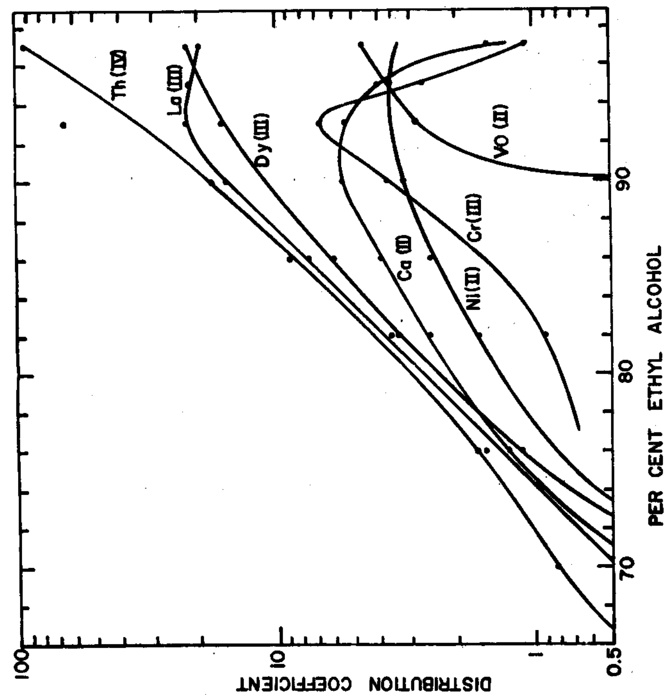

FIG. 12—Distribution coefficients of metal chlorides in 0·3M hydrochloric acid *vs.* percentage of ethyl alcohol. Low adsorption group.

Ni^{II}, Mn^{II}, Ca^{II} and Dy^{III} are eluted with 3*M* HCl-55% isopropyl alcohol.
Co^{II} is eluted with 1·3*M* HCl-55% isopropyl alcohol.
Cu^{II} and Fe^{III} are eluted with 0·1*M* HCl-55% isopropyl alcohol.
Zn^{II} is eluted with 0·005*M* aqueous HCl, or Bi^{III} is eluted with 1*M* aqueous sulphuric acid.

TABLE III.—SEPARATION AND ANALYSIS OF SYNTHETIC METAL ION MIXTURES ON DOWEX 1 × 8, 200- TO 400-MESH, CHLORIDE-FORM RESIN. METALS APPEAR IN THE ORDER OF ELUTION WITH THE AMOUNT OF WASH SOLUTION INCLUDED WITH THE FIRST ELUTED METAL.

Metal mixtures (column dimensions) and eluting agent	Taken, *mg*	Found, *mg*
Ni^{II}-Fe^{III}-Bi^{III} (6 × 2·2 cm)		
Ni 4 ml 95% EtOH-0·3*M* HCl		
50 ml 96% MeOH-0·2*M* HCl	8·96	8·93
Fe 45 ml 0·1*M* HCl-55% 2-PrOH	9·13	9·13
Bi 90 ml 1*M* aqueous H_2SO_4	8·66	8·50
Co^{II}-Fe^{III} (6 × 2·2 cm)		
Co 4 ml 95% EtOH-0·3*M* HCl		
60 ml 1·3*M* HCl-55% 2-PrOH	9·51	9·58
Fe 45 ml 0·1*M* HCl-55% 2-PrOH	9·13	9·12
Ni^{II}-Mn^{II}-Cu^{II} (6 × 2·2 cm)		
Ni 8 ml 95% EtOH-0·3*M* HCl		
47 ml 96% MeOH-0·2*M* HCl	8·96	8·94
Mn 80 ml 3*M* HCl-55% 2-PrOH	8·96	9·00
Cu 50 ml 0·1*M* HCl-55% 2-PrOH	8·94	8·89
Ni^{II}-Mn^{II}-Co^{II}-Cu^{II}-Zn^{II} (6 × 2·2 cm)		
Ni 8 ml 95% EtOH-0·3*M* HCl		
47 ml 96% MeOH-0·2*M* HCl	8·96	8·99
Mn 80 ml 3*M* HCl-55% 2-PrOH	8·96	8·88
Co 70 ml 1·3*M* HCl-55% 2-PrOH	9·51	9·50
Cu 50 ml 0·1*M* HCl-55% 2-PrOH	8·94	8·88
Zn 60 ml 0·005*M* aqueous HCl	8·95	9·06
Ni^{II}-Co^{II}-Cu^{II}-Bi^{III} (6 × 2·2 cm)		
Ni 8 ml 95% EtOH-0·3*M* HCl		
47 ml 96% MeOH-0·2*M* HCl	8·96	9·06
Co 65 ml 1·3*M* HCl-55% 2-PrOH	9·51	9·51
Cu 40 ml 0·1*M* HCl-55% 2-PrOH	8·95	8·97
Bi 85 ml 1*M* aqueous H_2SO_4	8·66	8·54
Dy^{III}-Mn^{II}-Cu^{II}-Fe^{III}-Bi^{III} (6 × 2·2 cm)		
Dy 8 ml 95% EtOH-0·3*M* HCl		
47 ml 96% MeOH-0·2*M* HCl	9·22	9·28
Mn 80 ml 3*M* HCl-55% 2-PrOH	8·96	8·99
Cu-Fe[a] 50 ml 0·1*M* HCl-55% 2-PrOH		
Cu	8·94	9·06
Fe	9·13	9·06
Bi 85 ml 1*M* aqueous H_2SO_4	8·66	8·66

TABLE III. (*contd.*)

Metal mixtures (column dimensions) and eluting agent		Taken, *mg*	Found, *mg*
Ni^{II}-Th^{IV}-Mn^{II}-Co^{II}-Cu^{II}-Fe^{III} (6 × 2·2 cm)			
Ni	8 ml 95% EtOH-0·3*M* HCl		
	73 ml 48% EtOH-48%*M* OH 0·2*M* HCl	8·96	8·99
Th	85 ml 96% MeOH-0·2*M* HCl	9·06	9·06
Mn	85 ml 3*M* HCl-55% 2-PrOH	8·95	8·96
Co	55 ml 1·3*M* HCl-55% 2-PrOH	9·51	9·56
Cu-Fe[a]	50 ml 0·1*M* HCl-55% 2-PrOH		
	Cu	8·94	8·96
	Fe	9·13	9·03
Ca^{II}-Mn^{II} (5 × 2·2 cm)			
Ca	2 ml 95% EtOH-0·3*M* HCl		
	56 ml 96% MeOH-0·2*M* HCl	8·33	8·40
Mn	80 ml 3*M* HCl-55% 2-PrOH	9·06	9·02
Ni^{II}-Mn^{II} (5 × 2·2 cm)			
Ni	2 ml 95% EtOH-0·3*M* HCl		
	56 ml 96% MeOH-0·2*M* HCl	4·45	4·51
Mn	80 ml 3*M* HCl-55% 2-PrOH	9·05	9·07

[a] Cu-Fe eluted together and analysed by a photometric titration[85] with EDTA as titrant.

This scheme gives sharp separations and virtually eliminates tailing of the bands. In Fig. 15 the elution curves are compared for the separation of nickel^{II} and cobalt^{II} by the isopropyl alcohol and the previous ethyl alcohol elution schemes. In the ethyl alcohol scheme, elution with 0·3*M* hydrochloric acid in 82% ethyl alcohol was continued after elution of the nickel until the cobalt break-through. In the isopropyl alcohol scheme, elution with 3*M* hydrochloric acid in 55% isopropyl alcohol was discontinued shortly after elution of the nickel was complete. At this point the cobalt band was still 4 cm from the bottom of the column, and the estimated cobalt break-through with the 3*M* eluent would be around 250 ml.

The isopropyl alcohol scheme does not offer a convenient separation of nickel^{II} or calcium^{II} from manganese^{II}. However, it was found that an excellent separation of nickel^{II} and manganese^{II} can be achieved through the use of 0·2*M* hydrochloric acid in 96% methyl alcohol (see Fig. 10). Although the distribution coefficient for manganese^{II} is only 27 in 0·2*M* hydrochloric acid-96% methanol (compared to a D of around 2000 in 0·3*M* hydrochloric acid-95% ethyl alcohol), column experiments showed that manganese^{II} is still strongly retained by a column. An elution curve for the column separation of nickel^{II} and manganese^{II} is given in Fig. 16. The curve shows sharp bands with very little tailing, and an excellent separation factor.

The recommended separation method is first to separate nickel^{II}, calcium^{II} or dysprosium^{III} from manganese^{II} (and other metal ions) using 0·2*M* hydrochloric acid in 96% methyl alcohol. The metal ions remaining on the column are then separated using the 55% isopropyl alcohol scheme outlined above. Fig. 17 shows elution curves for a multi-component mixture separated by this method, and Table III presents results

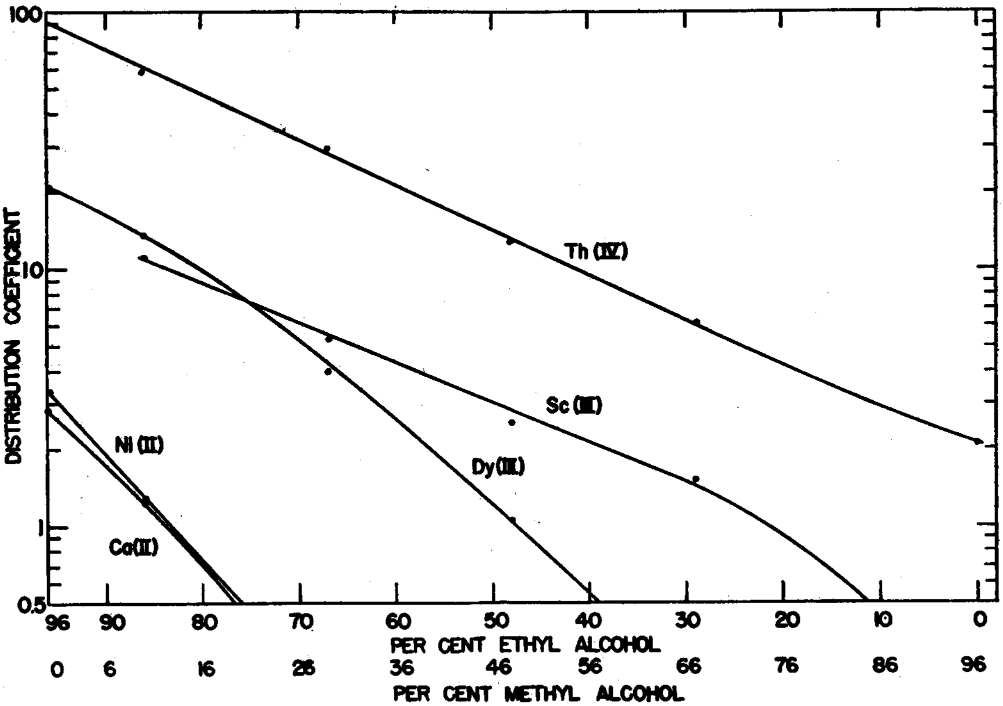

FIG. 13—Distribution coefficients of metal chlorides in 0·2*M* hydrochloric acid *vs.* concentration of methyl alcohol and ethyl alcohol totalling 96%.

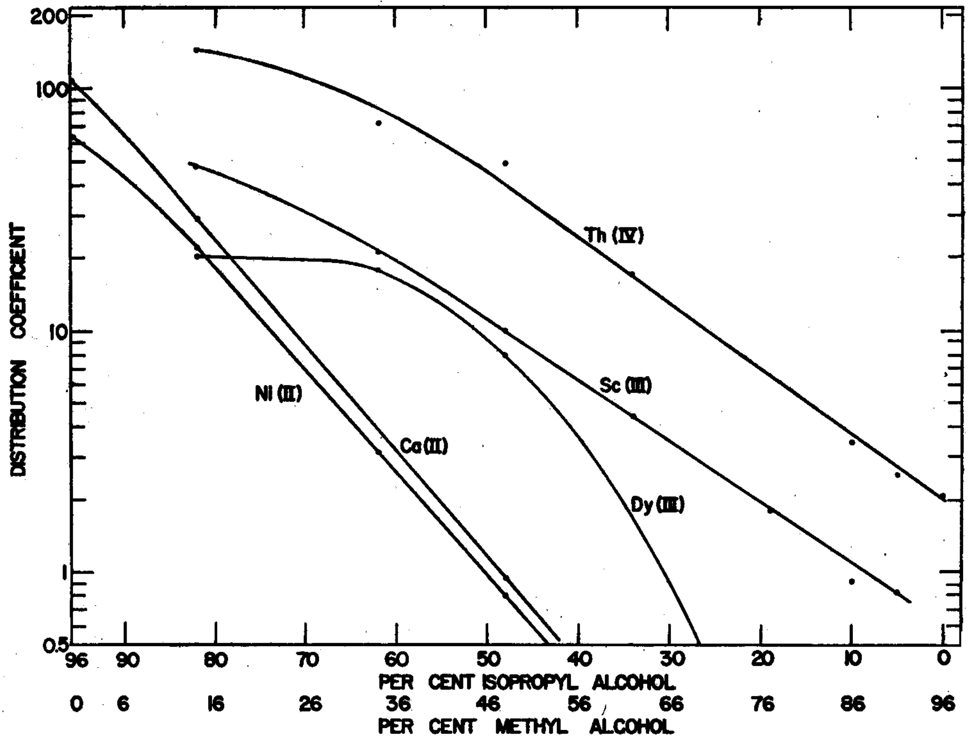

FIG. 14—Distribution coefficients of metal chlorides in 0·2*M* hydrochloric acid *vs.* concentration of methyl alcohol and isopropyl alcohol totalling 96%.

for the quantitative separation of several mixtures. It should be noted that a column of larger diameter was used for these separations than for those using 0·3*M* hydrochloric acid in ethyl alcohol (Table II). The larger column diameter allows greater loading and faster flow rates, but of course requires larger volumes of eluent for separation.

The distribution coefficient for thorium^{IV} is fairly high in 0·2*M* or 0·3*M* hydrochloric acid in 95% ethyl alcohol or isopropyl alcohol. Under these conditions the distribution coefficients of nickel^{II}, calcium^{II}, *etc.* are a little too high to permit a convenient separation from thorium^{IV}. However, Figs. 13 and 14 show that mixing methyl alcohol with isopropyl alcohol or ethyl alcohol provides a way to lower gradually the distribution coefficients of metal ions. In 0·2*M* hydrochloric acid-48% ethyl alcohol-48% methyl alcohol, a quantitative column separation of thorium^{IV} and nickel^{II} is obtained, although some tailing is observed in elution of the nickel. It appears that the use of mixed alcohols may also permit a fair separation of a nickel-dysprosium-thorium mixture.

TABLE IV.—SEPARATION AND ANALYSIS OF SYNTHETIC METAL ION MIXTURES ON DOWEX 1 × 8, 200- TO 400-MESH, CHLORIDE-FORM RESIN. (5 × 2·2 CM.). QUANTITIES AND TYPE OF ELUTING AGENT ARE SIMILAR TO THOSE IN TABLE III.

Metal mixture	Taken, *mg*	Found, *mg*
Co^{II}-Cu^{II}		
Co	38·46	38·40
Cu	4·46	4·45
Ni^{II}-Co^{II}		
Ni	35·46	35·48
Co	4·82	4·82
Co^{II}-Fe^{III}		
Co	38·46	38·49
Fe	4·63	4·64
Mn^{II}-Co^{II}		
Mn	36·22	36·39
Co	4·82	4·83
Ca^{II}-Mn^{II}		
Ca	33·34	33·36
Mn	4·51	4·60
Ni^{II}-Mn^{II}		
Ni	35·46	35·55
Mn	4·51	4·65

In the mixtures analysed above, the sample constituents are present in approximately equal molar amounts. In Table IV, results are reported for the successful analysis of mixtures where two components are present in approximately a 10 to 1 ratio. So long as the column is not overloaded, a high ratio of one or more sample constituents to the others does not appear to cause any difficulty.

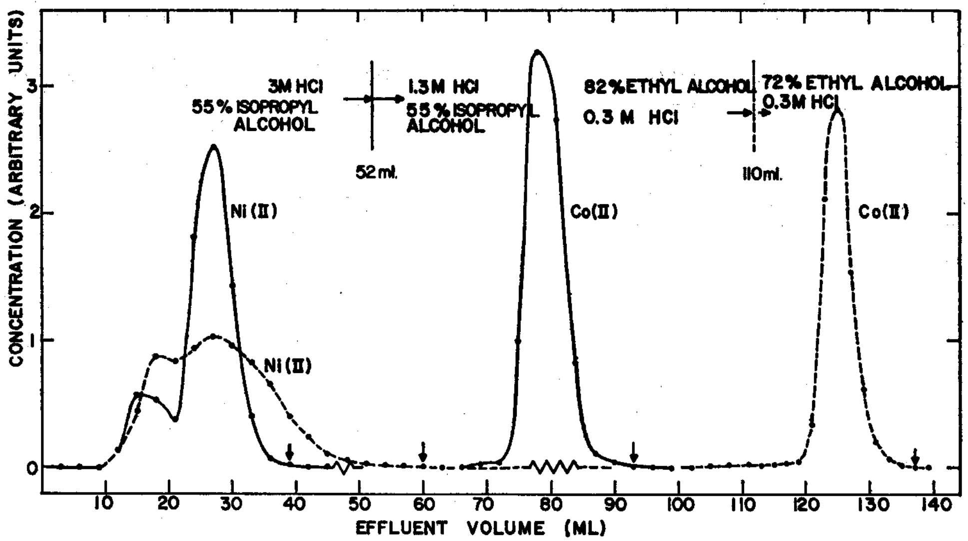

FIG. 15—Elution curves of a Ni^{II}-Co^{II} separation. Solid line represents elution by the varying hydrochloric acid-55% isopropyl alcohol eluting scheme. Dotted line represents elution by the varying percent of ethyl alcohol-0·3M hydrochloric acid eluting scheme. Flow rate of 1/4 to 1/3 ml/min and column dimensions of 5 × 2·2 cm (↓ = last detectable trace of metal ion.)

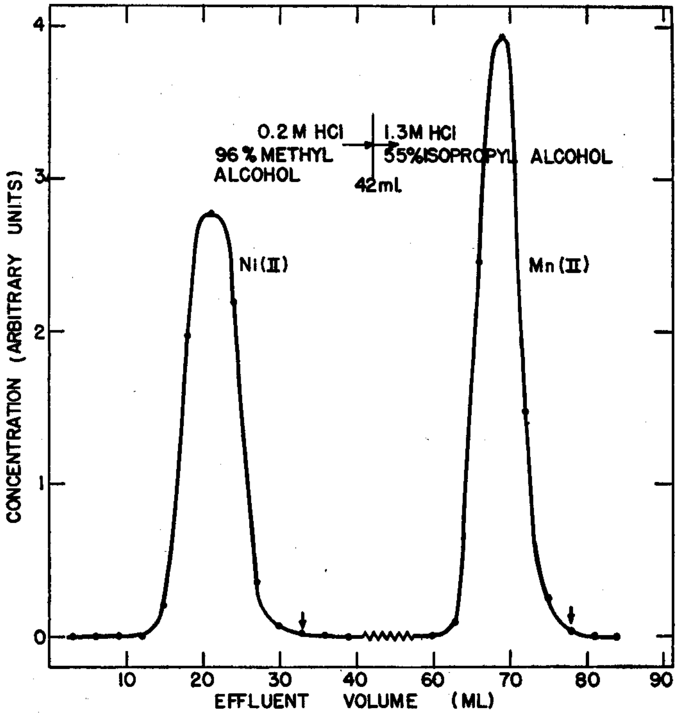

FIG. 16—Elution curve of a Ni^{II}-Mn^{II} separation. Flow rate of 1/4 to 1/3 ml/min and column dimensions of 6 × 2·2 cm. (↓ = last detectable trace of metal ion.)

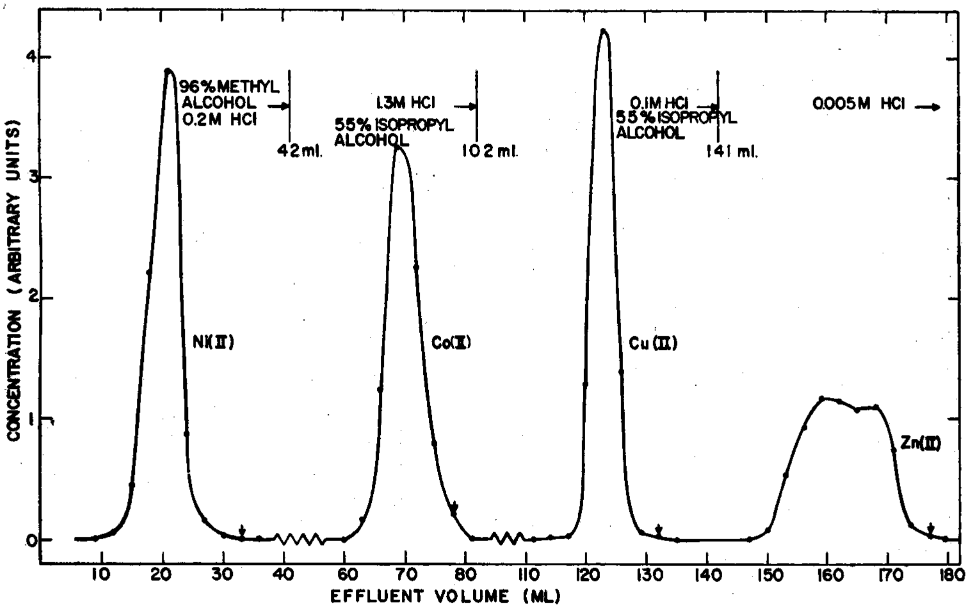

FIG. 17—Elution curve of a Ni^{II}-Co^{II}-Cu^{II}-Zn^{II} separation. Flow rate of 1/4 to 1/3 ml/min and column dimensions of 6 × 2·2 cm. (↓ = last detectable trace of metal ion.)

Zusammenfassung—Die Verteilungskoeffizienten für Metallionen zwischen einem Anionenaustauscher und einer flüssigen Phase (bestehend aus einer Mischung von Wasser und organischem Solvent), die Salzsäure enthält, wurden gemessen. Die Gegenwart von Salzsäure bewirkt, dass die Metallionen bei geringerer Säurekonzentration adsorbiert werden. In vielen Fällen sind die Verteilungskoeffizienten erheblich grösser als in Systemen mit wässriger Salzsäure. Bei sonst gleichen Bedingungen ist die Reihenfolge der Koeffizienten in Alkohol-Wasser-Salzsäure wie folgt: Isopropanol > Äthyl- > Methylalkohol. Säulentrennung von Metallionenmischungen können durchgeführt werden mittels Elution durch Alkohol-Wasser-Salzsäure-Mischungen verschiedener Zusammensetzung. Erfolgreiche Trennung einiger Gemische wird mitgeteilt.

Résumé—Les auteurs ont mesuré des coefficients de partage d'ions métalliques entre une résine échangeuse d'anions et des mélanges eau-solvant organique contenant de l'acide chlorhydrique. La présence d'un solvant organique provoque la fixation des ions métalliques à des concentrations d'acide chlorhydrique plus faibles. Dans de nombreux cas, les coefficients de partage sont beaucoup plus élevés que dans les systèmes eau-acide chlorhydrique. Les autres conditions étant comparables, l'ordre des coefficients de partage dans les mélanges alcool-eau-acide chlorhydrique est le suivant: alcool isopropylique, alcool éthylique, alcool méthylique. Les séparations sur colonne de mélanges d'ions métalliques peuvent être réalisées par élution avec des mélanges alcool-eau-acide chlorhydrique de différentes compositions. Des séparations d'un certain nombre de mélanges réalisées avec succès sont mentionnées.

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SHORT COMMUNICATIONS

The determination of iron with 1,10-phenanthroline

(*Received* 22 *August* 1960. *Accepted* 24 *September* 1960)

A COMPREHENSIVE study of the use 1,10-phenanthroline for the spectrophotometric determination of iron and the effect of interferences has been made by Fortune and Mellon.[1] However, the effect of interfering ions was presented from the standpoint of the optimum pH to be used when certain elements are present. To determine iron by the 1,10-phenanthroline method, it is desirable to know the effect of various ions at one particular pH. We have studied the extent of interference, if any, of 68 elements on the determination of 100 μg of iron, at pH 4·0. This particular pH was chosen because it seemed to be the optimum when the effects of all of the elements were considered.

EXPERIMENTAL

Procedure

To a 150-ml beaker were added a solution containing 10 mg of the element to be investigated, the standard iron solution (containing 100 μg of iron), 20 ml of 1*M* hydrochloric acid, 5 ml of 40% sodium acetate, and 2 ml of 10% hydroxylamine hydrochloride. The pH was adjusted to 4·0 ± 0·1 with a solution of sodium hydroxide and the solution was transferred to a 100-ml volumetric flask. Fifteen ml of 0·2% 1,10-phenanthroline were added and the solution was diluted to the mark. After 1 hr, the absorbance was measured at 510 mμ on a Cary Model 14 Recording Spectrophotometer, using 5-cm cells, with water as a reference. Samples containing precipitates were centrifuged before measuring. A number of elements precipitated either after the pH adjustment, or after the addition of 1,10-phenanthroline. The addition of citric acid before pH adjustment prevented precipitation in many instances and caused no interference, contrary to a published report.[2]

RESULTS

Elements which do not precipitate and do not interfere in the absence of citric acid

Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Zn, B, Al, Ga, In, Sc, Y, La, Si, Ge, Hf, As^{III}, V, Nb, Ta, F, Br, I, Mn^{II}, Mn^{VII}, Re, Pt, Ce^{IV}, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U^{VI}, P(as PO_4^{3-}; solutions containing P in 10-mg amounts must be allowed to stand overnight for complete colour development).

Elements which do not precipitate and do not interfere in the presence of 1 *g of citric acid*

Tl, Pb, Ti, Sb^{III}, Te, Bi, Sn, Zr, Mo, and W.

Elements which precipitate but do not interfere in the absence of citric acid

Au, Ba, Cd, Se, Ir (these elements also precipitated in the presence of citric acid) and Zr.

Elements which precipitate but do not interfere in the presence of 1 *g of citric acid*

Hg, Ir, Cd (solutions containing Cd in 10-mg amounts must be allowed to stand overnight for complete colour development).

Interfering elements

The following elements interfered, in 10-mg amounts, even in the presence of 1 g of citric acid. The percentage error in the determination of 100 μg of iron is indicated in parentheses. Cu(−100), Sn(−53), Cr^{III} (+15), Cr^{VI} (+15), Co (−37), Ni (−100), Rh (+22), Pd (+7). None of these elements interfered when present in 1-mg amounts. When 15 ml of 0·3% 1,10-phenanthroline were used, no interference was noted with 10 mg of Cu or Sn.

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Summary—The extent of interference of 68 elements in 10-mg amounts in the spectrophotometric determination of iron with 1,10-phenanthroline, was studied at pH 4. Using the procedure described, which uses 1 g of citric acid and 15 ml of 0·3% 1,10-phenanthroline, and allowing the coloured solutions to stand overnight before the absorbance is measured, only Cr^{III}, Cr^{VI}, Co, Ni, Rh and Pd interfere. None of the elements studied interferes in 1-mg amount.

Zusammenfassung—Das Ausmass der Störungen von 68 Elementen (anwesend in 10 mg Mengen) bei der Bestimmung von Eisen mit 1,10 Phenanthrolin bei pH 4 wurde studiert. Folgende Methode wurde verwendet: Die Farbe wird in einer Lösung entwickelt, die 1 g Citroenensäure und 15 ml 0·3% ige Reagenslösung enthält, wobei über Nacht stehen gelassen wird. Unter diesen Bedingungen stören lediglich: Cr(III), Cr(VI), Co, Ni, Rh und Pd. Keines der studierten Elemente stört, wenn nicht mehr als 1 mg anwesend ist.

Résumé—Les auteurs ont étudié à pH 4 l'importance de l'interférence causée par 68 éléments en quantité de 10 mg dans le dosage du fer par la 1,10-phénanthroline. En employant le procédé décrit qui utilise 1 g d'acide citrique, 15 ml de 1,10-phénanthroline à 0,3 pour cent, et en laissant reposer pendant une nuit les solutions colorées avant de mesurer l'absorption, seuls Cr (III), Cr (VI), Co, Ni, Rh et Pd gênent. Aucun des éléments étudies né gêne pour des quantités de 1 mg.

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Effect of nitric acid on the extraction of iron with tri-n-octylphosphine oxide

(*Received* 26 *August* 1960. *Accepted* 10 *October* 1960)

Recently, we published a method for the determination of iron in beryllium and beryllium oxide.[1] Because few elements interfere with the determination, we have applied the method to many different materials with considerable success. However, solutions which contain nitric acid from the dissolution of samples must be treated before the extraction of iron with tri-n-octylphosphine oxide (TOPO) in order to eliminate the deleterious effect of the nitrate ion.

With one exception no information is available concerning the effect of nitric acid on the extraction of iron with TOPO. White[2] states that iron is not extracted from $1M$ or $7M$ nitric acid. When it was found that the presence of nitric acid caused low results, the question arose: were the low results due to incomplete extraction of iron, or to the destruction by nitric acid of the colour-forming reagent, 1,10-phenanthroline? It has been established that nitric acid prevents the complete extraction of iron from a chloride medium with TOPO. This was established in the following manner. One ml of $15M$ nitric acid was added to 35 ml of $7M$ hydrochloric acid containing 100 μg of iron. This solution was extracted with $0{\cdot}01M$ TOPO in the usual manner. The aqueous phase was treated with a few drops of sulphuric acid, evaporated to dryness, and the iron determined by the aqueous 1,10-phenanthroline procedure; 45 to 50% of the iron originally added was found. The organic phase was treated with 3*M* sulphuric acid to remove the iron, and the acid solution evaporated to fumes of sulphuric acid to remove any nitrate. The acid solution was treated with hydrochloric acid and the iron extracted with TOPO and determined in the manner previously described;[1] 45 to 40% of the iron was found. The 90 to 95% recovery of iron is within expected experimental error. The results are adequate to prove that nitric acid interferes with the extraction of iron from a chloride medium by TOPO.

It should be pointed out that in White's report[2] it is stated that extraction of iron is 90% complete from 7*M* HCl containing 1*M* HNO_3. This lends additional experimental support to these conclusions.

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Summary—Nitric acid prevents the complete extraction of iron from a chloride medium with tri-n-octylphosphine oxide (TOPO).

Zusammenfassung—Es wurde gefunden, dass Salpetersäure die vollständige Extraktion von Eisen aus einem chloridhaltigen Medium mit Tri-n-octylphosphinoxyd stört.

Résumé—L'acide nitrique empêche l'extraction complète du fer par l'oxyde de tri-n-oxtylphosphine (TOPO) en milieu chlorure.

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LETTER TO THE EDITOR

RE: *J. Inorg. Nucl. Chem.*, 1959, **9**, 252; 1960, **11**, 124; 1960, **13**, 261, 269: *Talanta*, 1960, **3**, 219.

Sir:

I wish to acknowledge the contribution which Emeritus Professor H. T. S. Britton made to the above studies. The work was done in his former Department of Chemistry at University College, Exeter (now the University of Exeter). The programme was suggested by him and done under his direction and supervision, as required by the London University Ph.D. regulations for External Students.

I should like to record my gratitude to him for his guidance and criticism in this work, which is of course in his long-standing area of interest, and to express regrets for the previous omission of his name from these papers.

PETER CANNON

Alplaus, N.Y., U.S.A.
December 6, 1960

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BOOK REVIEWS

Advances in Inorganic Chemistry and Radiochemistry, Vol. 2. Edited by H. J. EMELEUS and A. G. SHARPE. Academic Press Inc., New York, 1960. Pp. viii + 392.

THIS volume, like the first, is an indispensable work of reference for research workers and teachers of inorganic chemistry. It comprises eight chapters, by contributors of world standing.

Much of the book is devoted to the covalent chemistry of sulphur, which has undergone remarkable developments in the last ten years. The chapter by O. Foss on "Structures of Sulfur Chain Compounds" and that by M. Becke-Goehring on "Amides and Imides of the Oxyacids of Sulphur" deal largely with one of the two main directions of advance, namely that concerned with the synthesis, structure and transformations of chain and ring sulphur compounds. Another rapidly expanding field, that of $-SF_5$ derivatives, is covered in G. H. Cady's "Fluorine-containing Compounds of Sulphur."

J. D. Dunitz and L. E. Orgel contribute a chapter on "The Stereochemistry of Ionic Solids" in which the impact of the ligand field theory on classical conceptions of ionic crystal structures is discussed fully and with exceptional clarity. F. G. A. Stone's "Chemical Reactivity of the Boron Hydrides" and J. J. Katz and I. Sheft's "Halides of the Actinide Elements" are both valuable contributions of unusual character. J. Eisch and H. Gilman's "Organometallic Compounds" is a survey of recent advances in methods of operation in this field of chemistry, and of new principles and generalisations which have lately emerged. The only article on nuclear chemistry is "Mass Spectrometry in Nuclear Chemistry" by H. G. Thode, C. C. McMullen and K. Fritze. It embodies the results of more than a decade of patient and unobtrusive work without which our present understanding of nuclear reactions could not have been acquired.

All the chapters cover the literature through 1958, in some cases into 1959, except "Fluorine-containing Compounds of Sulphur" which is only complete through 1956. Unfortunately, therefore, the recent spectacular developments in sulphur tetrafluoride chemistry are not mentioned at all.

H. G. HEAL

X-Ray Powder Photography in Inorganic Chemistry, R. W. M. D'EYE and E. WAIT. Butterworths Scientific Publications, London, 1960. Pp. viii + 222. 45s.

THIS book has been written to provide the research chemist, having no experience of crystallography, with the essential information to enable him to use the powder technique to the best advantage in his work.

Chapters are included on the production and isolation of the necessary monochromatic X-ray beam, on the design and calibration of the Debye-Scherrer camera and the several focusing types of camera, and on sample preparation. Much useful practical advice is given and the techniques available are compared as to suitability for various applications.

The usual aim of the powder technique is to characterise the crystal system of the compound examined and determine the lattice parameters accurately. The authors give a comprehensive survey of the graphical and analytical methods available for extracting this information from a powder pattern. Many worked examples make these two chapters a most valuable part of the book.

A chapter on crystallographic theory discusses the properties of two and three dimensional lattices and relates these to the symmetry found in crystals. The various symmetry elements are explained and their combination into a space group to describe a particular crystal symmetry is discussed.

A detailed treatment of the factors affecting the intensity of a diffraction line is given. This is followed by a section on determination of atomic positions in the unit cell. Three examples, of a highly symmetrical structure with positions fixed by symmetry and of less symmetrical structures with one or more parameter variable, are used to discuss this topic in a most useful and practical way.

A long chapter on applications concludes the book. Some topics dealt with are qualitative and quantitative analysis, determination of chemical formulae, study of semiconductors, anomalous mixed crystals, solid-solid reactions. A good index makes it easy to refer to any specific topic and adequate and up-to-date references are collected at the end of each chapter.

The book should prove a valuable addition to the library of any crystallographer, chemist or physicist. It is written in a practical way, the style is concise but nowhere is accuracy sacrificed to brevity. The treatment is fresh and should stimulate the interest of readers in the technique. The authors have obviously put into the book the results of their own experience as chemist-crystallographers. They have succeeded in writing a book self-evidently founded on a thorough acquaintance with their subjects.

B. J. McDonald

Advances in Fluorine Chemistry, I. Edited by M. Stacey, J. Tatlow and A. G. Sharpe. London. Butterworth's Scientific Publications, 1960. 45s.

Until the present book came out, Volume I of the "Mellor" supplement, now nearly five years old, contained the most recent comprehensive general account of fluorine chemistry. Five years are a long time in the history of this element, and the need for a good new textbook has been getting more and more pressing. Since the task of writing up fluorine adequately is now almost beyond the capacity of any one person or small group, it has been decided to publish a continuing series of collective volumes, of which this is the first. It is planned to cover both fundamental and industrial developments. Fluorocarbon chemistry alone, potentially as large as the field of organic chemistry itself, could ensure an adequate supply of material for many future volumes.

All the contributors to Volume I are experts of international reputation. The book is throughout interesting, topical, up-to-date and fully documented. The following subjects are dealt with: halogen fluorides: transition metal fluorides and their complexes; fluoroboric acids and their derivatives; electrochemical fluorination; and fluorination with high-valency metallic fluorides.

This is a very useful and reasonably priced book.

H. G. Heal

Elementary Titrimetric Analysis. A. M. G. Macdonald. Butterworth, London, 1960. pp. viii + 133. 12s. 6d.

This little book is a well-balanced presentation of titrimetric methods for school and technical college students beginning their serious study of quantitative analysis.

Short introductory chapters deal competently with nomenclature and with the use and maintenance of apparatus. Sections on acid-base titrations, argentimetric methods, redox titrations and complexometric titrations are each based on a sound discussion of principles and the procedures are indicated in a nicely-varied selection of exercises. The theory of redox titrations, in particular, is admirably expounded in relation to the use of permanganate, dichromate, ceric sulphate, mercurous nitrate and iodimetric methods.

In a book which attempts so much within its 123 pages of text, it is perhaps inevitable that the treatment is sometimes rather dogmatically concise. Fuller descriptions of some of the procedures and more detailed guidance on the recording of results are desirable at this level. Many teachers, mindful of the pitfalls of a rule-of-thumb approach to titrimetric calculations, will not share the author's enthusiasm for $v_1n_1 = v_2n_2$ and would welcome more attention to exercises which aim at facility in the manipulation of gram-equivalents. There are a few inconsistencies, as when the author stresses the value of a high equivalent weight in a standard substance, yet occasionally specifies quantities which are unrealistically small for elementary work; and when her description of the neutralisation curve of phosphoric acid goes beyond what can be seen in her diagram. But these are minor blemishes in an excellent book. The student who uses it will proceed with confidence to any of the standard works mentioned in the short bibliography.

The book is well printed and strongly bound. A few additional pages in a subsequent edition would enable the author to improve the exposition in places and thereby increase the usefulness of the book to students.

J. McG. Jackson

The Routine Analysis of Copper Base Alloys. Frank J. Versagi. Chemical Publishing Co. Inc., New York, 1960. pp. 168 $5.00

This slim volume is a collection of methods of analysis likely to prove useful to those for whom the author states it is intended. Even though "theroretical" chemistry has been deliberately excluded as far as possible, it is disquieting to find to be inaccurate some of the little there is. For example on p. 70 we are told that aluminium precipitates from a solution made alkaline with 10 ml of saturated caustic soda solution, and on p. 71 that "boiling with sodium hydroxide drives off the nitric acid." The statement on p. 15 that for routine work it is never necessary to weigh beyond four significant figures is obviously nonsense when electrolytic methods are used as often as in copper alloy analysis. On the practical side, one may ask what is the purpose and effect of adding 1 drop of 0.1*N* hydrochloric acid to the electrolyte before determining copper (p. 30).

The book is not free from typographical errors, the worst being the misplacement of a whole line on p. 157, and the consistent use throughout of Mu for mμ. Although the book undoubtedly achieves its avowed aims, one wonders whether they are completely desirable ones or whether it would be better to follow Hillebrand in wishing to produce analytical chemists rather than chemical analysts. Finally, five dollars seems a lot to pay for 168 pages, 20 of which are completely blank, being unsullied even by the page numbers they should bear.

R. A. Chalmers

Talanta, 1961, Vol. 8, p. 170. Pergamon Press Ltd. Printed in Northern Ireland

TALANTA MEDAL

THE Editorial Board and Publishers of TALANTA take pleasure in announcing that with the approval of the Advisory Board they recommend the first award of the Talanta Medal to

PROFESSOR FRITZ FEIGL.

Through the kind co-operation of the organisers of the forthcoming Congress on Analytical Chemistry in Budapest on April 24–29, 1961, it is proposed that the award will be made to Professor Feigl at that meeting.

PROFESSOR FEIGL is famous for his "spot tests." These sensitive colour and precipitation reactions have been used to detect traces of various inorganic and organic materials. In itself this work is amongst the most notable contributions to analytical chemistry of the past two generations; but it is unfortunate that the fundamental ideas behind Feigl's work have, on the whole, been overlooked. In many cases Feigl has discovered these reactions himself, and this alone constitutes a chemical contribution of the first rank.

The colour reactions in turn have formed the basis for quantitative determinations by later workers, and in many cases the discoverer has been overlooked. The vast development of paper chromatography would have been seriously impeded had not Feigl's spot tests been available for detecting separated components. Feigl was probably the first to place the use of masking reactions on a scientific basis, and many of the reactions which he uses in his spot tests to overcome the effects of interfering ions have been adapted to use in many other analytical processes. Again he has received little credit for this.

These are just a few examples of the great impact that his work has had on modern analytical chemistry. He is undoubtedly one of the great living analytical chemists; his study of reactions has been a life-time's work; and probably no-one has contributed so many new reactions to the whole field of chemistry. His work has been going on continuously for nearly fifty years. His results have been applied in fields as far apart as qualitative testing, paper chromatography and spectrophotometry. It is felt that he is a most worthy recipient of the Medal.

Talanta, 1961, Vol. 8, pp. 171 to 172. Pergamon Press Ltd. Printed in Northern Ireland

EDITORIAL NOTE

THE present issue of TALANTA marks a stage in the Journal's development which, we feel, requires some comment.

In the first place, the Editor would like to thank all his subscribers and contributors for their patience during the teething troubles of a new Journal. Teething troubles are inevitable, but are not always sufficiently appreciated to be tolerated with indulgence. The fact that, in general, both contributors and subscribers have shown an understanding of the difficulties has been a kindness which has been more recognised by the Editor than acknowledged.

This issue, which is to some extent anomalous in being a double issue, should appear in the first week of March. From this point onwards, we hope that each issue will appear monthly in the month listed on the cover. This is a state of affairs which our subscribers and contributors will be only too well aware has not occurred in the past.

Qui s'excuse, it is said, *s'accuse:* but when the decision was taken, in September 1959, to change, in January 1960, from bimonthly to monthly appearance, both editorial and printing difficulties had to be overcome. In consequence, our publication dates during 1960 were, to say the least, erratic, and in general long overdue; although on this point we feel that our subscribers had more complaint than our contributors, since the actual time from acceptance to publication has not, on the whole, been unduly protracted.

As we emerged from the difficulties arising from the change in time-schedule, we became involved—very willingly, but to the detriment of our normal programme—in the production of the special issue in honour of Professor Willard, which has just appeared. This called for additional work, both on the editorial side and with the printer. The special Gatlinburg volume was a further strain on the printer, although editorial headaches were nominal, since our American colleagues made themselves responsible for these.

At this point it is only appropriate to acknowledge the co-operation that has been given throughout by our printers, whose patience we must frequently have strained almost (although fortunately never quite) to breaking point.

Rather belatedly, we would take this opportunity to explain the new system of volume numbers. Up to the present there have been three volumes per year, and since we commenced on a bimonthly basis in the middle of a year, this has resulted in non-coincidence of years with volume numbers. From January 1961, we propose to adhere to the more usual "one year, one volume" basis, so that the 1961 volume will be Volume 8, and will comprise twelve issues. Volume 7, which began with the November-December 1960 issue, has been completed by the special Willard issue (which in itself is rather larger than an average double issue). Volume 6 was the special Gatlinburg issue, and Volume 5 is made up by the July-October 1960 issues.

In conclusion, we would like to reiterate that from this issue forward we expect to publish in the first week of the appropriate month. It may be necessary, from time to time, to close matter for press with a reduced number of pages. But this will be offset by additional pages in other issues, so that the average number of pages per issue will remain as before.

In the near future we hope, in response to requests, to give some account of our editorial and refereeing policy. At the moment we would merely draw the attention of our readers to the recently revised Notes for Contributors, which we expect, on that occasion, to comment on at more length.

Talanta, 1961, Vol. 8, pp. 173 to 174. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged

Friday 3 *March* 1961: **Society for Analytical Chemistry:** Annual General Meeting, 2.15 p.m., and Address of Retiring President, Mr. R. C. CHIRNSIDE, F.R.I.C. *The Enlargement of Horizons in Analytical Chemistry.* 2.45 p.m. Burlington House, London, W.1.

Biennial Dinner. Fishmonger's Hall, London Bridge, London, E.C.4. 7.15 p.m. for 7.45 p.m.

Wednesday 8 *March* 1961: **Society for Analytical Chemistry,** Midlands Section: *Some Newer Reagents in Analytical Chemistry:* Professor R. BELCHER, D.Sc., F.R.I.C. The Technical College, Luton. 6.30 p.m.

Friday 10 *March* 1961: **Society for Analytical Chemistry,** Western Section and **Royal Institute of Chemistry,** South Wales Section: Joint Meeting: *Vapour Phase Chromatography:* Mr. A. VERDIN. Swansea.

Tuesday 14 *March* 1961: **Society for Analytical Chemistry,** Midlands Section: Annual General Meeting. Regent House, Birmingham. 6.30 p.m.

Wednesday 22 *March* 1961: **Society for Analytical Chemistry,** Microchemistry Group: Discussion Meeting. *The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Thursday 23 *March* 1961: **Society for Analytical Chemistry,** Midlands Section: *Measurement of pH and Electrode Potential for Analytical Purposes:* Dr. G. MATTOCK. The Technical College, Nottingham. 7.00 p.m.

Friday 24 *March* 1961: **Society for Analytical Chemistry,** Scottish Section: *Non-aqueous Titrimetry:* Mr. G. R. JAMIESON, B.Sc., A.R.I.C. and Dr. E. R. LANE, F.R.I.C. Glasgow.

Saturday 25 *March* 1961: **Society for Analytical Chemistry,** Physical Methods Group and North of England Section: Joint Meeting: *The Analysis of Intact Samples.* City Laboratories, Mount Pleasant, Liverpool. 2.15 p.m.

Wednesday 29 *March* 1961: **Society for Analytical Chemistry:** Demonstration Meeting of Laboratory-Built Equipment. Chelsea College of Science and Technology, Manresa Road, London, S.W.3.

Thursday 6 *April* 1961: **Society for Analytical Chemistry,** Biological Methods Group: Discussion Meeting: *Principles Involved in Collaborative Studies*: Mr. S. A. PRICE, B.Sc., F.R.I.C. *The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Wednesday 12th *April* 1961: **Society for Analytical Chemistry** and **Oil and Colour Chemists Association:** Joint Meeting. Wellcome Building, Euston Road, London, N.W.1. 7.00 p.m.

Wednesday 26 *April* 1961: **Society for Analytical Chemistry,** Midlands Section and Physical Methods Group: Joint Meeting: *Spectrofluorimetry:* Dr. C. A. PARKER. *Tesla Luminescence:* Dr. R. J. MAGEE. University, Edgbaston, Birmingham, 15. 7.00 p.m. Preceded by a visit to the Mond Nickel Co. Ltd. 3.00 p.m.

Friday 28 *April* 1961: **Society for Analytical Chemistry,** Western Section and **Society for Chemical Industry,** South Wales Section and Food Group: Joint Meeting: *Modern Legislation in Relation to Food Additives:* Mr. C. A. ADAMS, C.B.E., B.Sc., F.R.I.C. Cardiff.

Friday 28 *April* 1961: **Society for Analytical Chemistry,** North of England Section and Scottish Section: Joint Meeting: *Ion Exchange:* Dr. T. R. E. KRESSMAN, F.R.I.C. *The Determination of Nitrates with Particular Emphasis on the Use of Dead-stop Titrimetry:* Mr. A. F. WILLIAMS, B.Sc., F.R.I.C. Central Hotel, Victoria Viaduct, Carlisle. 7.15 p.m.

(*Monday–Tuesday* 8–9 *May* 1961: Analytical Chemistry Subject Division and the Cornwall Ontario) District Section of the **Chemical Institute of Canada:** *Symposium on Titrimetric Methods of Analysis.* Parkway Hotel, Cornwall, Ontario.

The symposium will consist of three half-day sessions, each of which will be devoted to one of the following subjects: *Complexometric Titrations, Titrations in Non-aqueous Media* and *Electrometric Titrations.* Professor J. S. FRITZ, Professor G. N. REILLY and Dr. G. BUC will be delivering lectures covering these three aspects of titrimetric analysis.

Enquiries should be addressed to Mr. J. R. MCCALLUM, Courtaulds (Canada) Ltd., Cornwall, Ontario.

Tuesday–Saturday 19–23 *September* 1961: Analytical Commission of the Chemical Committee of the **Polish Academy of Sciences** with the collaboration of the **Polish Chemical Society** and the **Institute of Nuclear Research:** *Third Polish Conference on Emission Spectral Analysis.* Jelitkowo near Gnańsk.

The conference will be devoted to theoretical and experimental works performed recently in the field of emission spectral analysis, and its application to research and industry.

The general programme is as follows:

1. *General problems: apparatus, excitation sources, interpretation of results, etc.*
2. *Spectral analysis of metals.*
3. *Spectral analysis of non-conducting samples.*
4. *Spectral analysis of solutions, including flame photometry.*
5. *X-ray emission and X-ray fluorescence analysis.*

Lectures will be held in Polish, English, Russian or German, and all papers will be published in a special edition of *Chemia Analityczna.*

Enquiries should be addressed to Mgr. ADAM HULANICKI, Komisja Analityczna, Komitsetu Nauk Chemicznych PAN, Warsawa 22, Pasteura I, Poland.

B.S.I. News announces the following new British Standards:

B.S. 3279: *Seedlac:* 1960. This supersedes the relevant parts of B.S. 954, 'Lac'. Provision is made for six grades which correspond approximately to six grades in ISO/R 55 'Seedlac' and which differ in matter insoluble in hot alcohol, non-volatile matter soluble in cold alcohol and colour index. The scope, description, sample, volatile matter, matter insoluble in hot alcohol and method of expressing the analytical results are specified. Optional clauses, covering the requirements of different users, are for colour index, matter soluble in water, non-volatile matter soluble in cold alcohol and wax. (Price 5s.)

B.S. 3280: *Hand-made shellac:* 1960. This supersedes the relevant parts of B.S. 954, 'Lac'. Provision is made for five grades which correspond approximately to the top five out of six grades in ISO/R 55 'Shellac' and which differ in matter insoluble in hot alcohol, non-volatile matter soluble in cold alcohol, colour index and ash. The scope, appearance and colour, sample, matter insoluble in hot alcohol, orpiment, rosin and method of expressing the analytical results are specified. Optional clauses, covering the requirements of different users, are for colour index, volatile matter, matter soluble in water, non-volatile matter soluble in cold alcohol, ash, grit wax, flow, life under heat, acid value, iodine value, arsenic and lead. (Price 10s.)

The following Amendment Slip is also announced:

B.S. 1728: *Methods for the analysis of aluminium and aluminium alloys: Part* 2 1952: *Determination of magnesium.* Amendment No. 2: PD 3886. (Gratis)

Talanta, 1961, Vol. 8, pp. 175 to 176. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Selection of complexing agents for complexometric titrations: Erkki Wänninen. (21 *November* 1960).

Determination of water by near infrared spectroscopy: D. A. Keyworth. (21 *November* 1960).

Metallochromic indicators—X: A new mixed indicator for the chelatometric determination of calcium: V. Svoboda, V. Chromý, J. Körbl and L. Dorazil. (23 *November* 1960).

Thermogravimetric decomposition of thorium 8-hydroxyquinolate: C. E. Crouthamel and C. E. Johnson. (28 *November* 1960).

Spectrophotometric determination of palladium with nitrilo-acetic acid: P. G. Desideri and F. Pantani. (29 *November* 1960).

The anion-exchange separation of technetium, rhenium and manganese: Miroslav Pirs and Robert J. Magee. (30 *November* 1960).

Potentiometrische Titrationen—I: Allgemeine Betrachtungen und die Theorie chelatometrischer Titrationen ohne Anwendung eines Indicators: H. Flaschka. (7 *December* 1960).

Murexide (ammonium purpurate) as an indicator in thorium-ethylenediaminetetra-acetic acid titrations: Satandra Prashad Sangal and Arun K. Dey. (12 *December* 1960).

Mitteilung über quantitative organische Analyse—XXVIII: Eine automatische Methode zur Mikrobestimmung von Kohlenstoff, Wasserstoff und Stickstoff: M. Vecera. (14 *December* 1960).

Applications de la chélatometrie—VII: Dosage volumétrique des *o*-acyl-phènols. Claude Hennart et (Mme.) Yvette Lefevre. (15 *December* 1960).

Spectrophotometric study of the complex of lanthanum and Alizarin Red S: Toshi Kawashima, Haruno Ogawa and Hiroshi Hamaguchi. (19 *December* 1960).

Spectrophotometric determination of thorium in low-grade minerals and ores: Anna-Lisa Arnfelt and Inga Edmundsson. (19 *December* 1960).

New colour reactions of elemental sulphur and carbon disulphide: T. Urbánski. (19 *December* 1960).

Use of "tagged" atoms for the investigation of precipitate exchange reactions: L. Erdey, D. Hegedus and I. Porubszky. (2 *January* 1961).

Organic analysis—XXIX: A new spraying reagent for reducing sugars on paper chromatograms: Tsutomu Momose and Masaru Nakamura. (2 *January* 1961).

Fluorometric determination of zirconium with quercetin: Separation of interference by extraction with TTA: David M. Hercules. (3 *January* 1961).

Determination of fluorine in mineral waters using Xylenol Orange: Roman Valach. (4 *January* 1961).

Salting-out chromatography—VII: Analysis of mixtures of dialkylphosphoric acids, alkane phosphonic acids and orthophosphoric acid: F. Jakob, K. C. Park, J. Ciric and Wm. Rieman III. (6 *January* 1961).

Titrimetric determination of vanadium^{III} with sodium metavanadate using oxidation-reduction indicators: B. V. S. R. Murthy snd G. Gopala Rao. (9 *January* 1961).

The latent heat of fusion of ethylene carbonate: R. F. Kempa and W. H. Lee. (10 *January* 1961).

The spectrophotometric determination of the ionisation constants of some derivatives of barbituric acid: MURRAY E. TAYLOR and REX J. ROBINSON. (10 *January* 1961).

Applications de la chélatométrie—IX: Semi-microdosage de l'iode dans les substances organiques en présence des autres halogènes: CLAUDE HENNART. (13 *January* 1961).

Extraction of arsenic^{V} from H_2SO_4-KBr solutions and its analytical use: K. STUDLAR. (16 *January* 1961).

Colour reactions of some 1,4-dihydroxyanthraquinones with aluminium and beryllium: E. GUY OWENS II and JOHN H. YOE. (16 *January* 1961).

Homogeneous precipitation from mixed solvents: LESTER C. HOWICK and JERRY L. JONES. (16 *January* 1961).

The determination of thiomalic acid: A. I. BUSEV and SHAN FAN. (17 *January* 1961).

The consecutive radiometric titration of several elements using the sodium salt of 1-dithiocarboxy-3-methyl-5-phenylpyrazoline containing sulphur-35: A. I. BUSEV and V. M. BYRKO. (17 *January* 1961).

Contributions to the basic problems of complexometry—V: Mutual masking of iron and manganese: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (19 *January* 1961).

Isotopic dilution analysis by solvent extraction—III: Highly selective determination of trace amounts of mercury: JAROMÍR RŮŽIČKA and JIŘÍ STARY. (19 *January* 1961).

Titrimetric determination of titanium^{III} with sodium metavanadate—I: Use of neutral red, phenosafranine or safranine-T as oxidation-reduction indicators: B. V. S. R. MURTHY and G. GOPALA RAO. (23 *January* 1961).

Potentiometric titration of titanium^{III} with vanadium^{IV}: B. S. V. R. MURTHY and G. GOPALA RAO. (23 *January* 1961).

Titrimetric determination of indigo sulphonate with potassium iodate: G. GOPALA RAO and N. VENKATESWARA RAO. (23 *January* 1961).

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiased reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. **Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced.** Where possible, research papers should follow the pattern: *Introduction*, *Discussion*, *Conclusion*, *Experimental* (or such of these headings as apply.)

3. Because the bulk of material will be set directly in page proof, every attempt should be made to ensure that before being submitted, manuscripts are essentially in the final form desired by the authors, and that no alterations of moment will be required at the proof stage. Alterations suggested by the referee will be agreed with the authors at the manuscript stage. Authors whose native language is not English are advised that in submitting papers in English they should endeavour to have the paper thoroughly corrected before submitting for publication. If the manuscript requires considerable editing, it may have to be returned to the authors for re-typing, resulting in a serious delay in publication.

4. The essential contents of each paper should be briefly recapitulated in a summary placed at the beginning of a paper, or at the end of a preliminary or short communication. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

5. Illustrations should be separate from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, since they are easily available to the printers:

▲ △ ⊡ □ ● ○ ◬ ⊙ ⊕ ⊖ ⌽ ⊗

6. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, *e.g.*, standard deviation. The same information should not be reproduced in both tables and figures.

7. The preferred positions for all figures and tables should be indicated in the manuscript by the authors.

8. **References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:**

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

9. Except in the case of preliminary communications, proofs will be sent out to authors for correction. For papers these will be in page form. **It is emphasised that at this stage extensive alterations to the text or failure to return the corrected proofs promptly may result in serious delay in publication.**

10. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units. In editing papers for publication the conventions used, on the whole, will be English spelling for all matter in the English language, and the general usages described in *Handbook for Chemical Society Authors* (The Chemical Society, London, Special Publication No. 14, 1960). It would be helpful if authors would consult this for guidance in the preparation of their manuscripts. (Authors who wish to retain American spelling, or to adhere to other generally accepted usages, should indicate this clearly at the time of submission of the manuscript.)

11. Where several authors are involved in a paper, an indication of the author to whom requests for reprints should be addressed may be given by placing the symbol ® after the name of that author.

By following the Script Requirements carefully, authors will assist greatly in ensuring rapid publication.

FEBRUARY–MARCH 1961 VOLUME 8 NUMBERS 2/3

CONTENTS

Short Communications

Letter to the Editor

PERGAMON PRESS LTD.

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